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1932









# TRANSACTIONS

OF THE

## AMERICAN INSTITUTE OF MINING AND METALLURGICAL ENGINEERS

(INCORPORATED)

Vol. 99

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## INSTITUTE OF METALS DIVISION 1932

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PAPERS AND DISCUSSIONS PRESENTED BEFORE THE DIVISION AT MEETINGS HELD  
AT BOSTON, SEPTEMBER, 1931, AND AT NEW YORK, FEBRUARY, 1932

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## *Notice*

This volume is the sixth of a series constituting the official proceedings of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers. It deals with nonferrous metals and includes papers presented at the Boston Meeting, Sept. 21-25, 1931, and the New York Meeting, Feb. 15-18, 1932.

The series is a continuation of the publications and proceedings of the Institute of Metals Division. The complete list of publications and proceedings, including the present volume, is as follows:

1908-1911 *Transactions of the American Brass Founders' Association*: 1908, Vols. 1 and 2; 1909, Vol. 3; 1910, Vol. 4; 1911, Vol. 5.

1912-1916 *Transactions of the American Institute of Metals*, Vols. 6-10.

1917-1918 *Journal of the American Institute of Metals*, Vols. 11-12.

1919-1926 *TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers*, Volumes 60, 64, 67, 68, 69, 70, 71 and 73.

1927-1928 *PROCEEDINGS of the Institute of Metals Division of the American Institute of Mining and Metallurgical Engineers*, two volumes, of which the latter is now designated Vol. 78 of the A. I. M. E. *TRANSACTIONS*.

1929-1932 *TRANSACTIONS of the American Institute of Mining and Metallurgical Engineers*, Volumes 83, 89, 93 and 99, Institute of Metals Division

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## Resumption of Serial Numbers for the Transactions

WITH this volume of the TRANSACTIONS is resumed the serial numbering that was discontinued after the issuance of Volume 76 in 1928. The designation of the present volume therefore is TRANSACTIONS A.I.M.E., Vol. 99, Institute of Metals Division, 1932. The following table shows the existing titles of the volumes published in the interval and also the supplemental designations. Likewise are shown the complete designations of the volumes yet to be issued in 1932. Anyone desiring to revise the designations on the backbones of his volumes can obtain appropriate stickers with gilt letters, to match the binding, at small cost by addressing the office of the Secretary.

PRESENT TITLE OF VOLUME	ADDITIONAL DESIGNATION
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GEOPHYSICAL PROSPECTING, 1929.	TRANS. A.I.M.E. Vol. 81
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## The Institute of Metals Lecture

AN annual lectureship was established in 1921 by the Institute of Metals Division, which has come to be one of the important functions of the Annual Meeting of the Institute. A number of distinguished men from this country and abroad have served in this lectureship. The roll is quoted below:

- 1922 Colloid Chemistry and Metallurgy. By Wilder D. Bancroft.
- 1923 Solid Solution. By Walter Rosenhain.
- 1924 The Trend in the Science of Metals. By Zay Jeffries.
- 1925 Action of Hot Wall: a Factor of Fundamental Influence on the Rapid Corrosion of Water Tubes and Related to the Segregation in Hot Metals. By Carl Benedicks.
- 1926 The Relation between Metallurgy and Atomic Structure. By Paul D. Foote.
- 1927 Growth of Metallic Crystals. By Cecil H. Desch.
- 1928 Twinning in Metals. By C. H. Mathewson.
- 1929 The Passivity of Metals, and Its Relation to Problems of Corrosion. By Ulick R. Evans.
- 1930 Hard Metal Carbides and Cemented Tungsten Carbide. By S. L. Hoyt.
- 1931 X-ray Determination of Alloy Equilibrium Diagrams. By Arne Westgren.
- 1932 The Age-hardening of Metals. By Paul D. Merica.

## FOREWORD

THIS volume of the TRANSACTIONS, which is the sixth of the separate Institute of Metals series and contains papers presented at the October (1931) meeting in Boston and the February (1932) meeting in New York, gives evidence that the Institute of Metals Division in its publications is serving a wide range of interests, covering both theory and practice, in its expansive field of nonferrous metals and alloys.

In addition to papers which contribute to the development of such fundamental subjects as microscopic metallography, the constitution of alloys, corrosion, and metal testing and technology, the volume includes papers and discussions on such timely topics as age-hardening, admirably reviewed by Dr. Paul D. Merica in the annual (February) lecture of the Division, and various applications of X-ray metallography to both theoretical and practical problems.

The titles of all papers accepted for publication by the Division during the year are listed in the table of contents (and index). A statement defining the form in which it was issued follows the title of each paper not included in the volume.

Papers sponsored by the Institute of Metals Division at a joint session with the Iron and Steel Division on Gases in Metals, held February 16, have been held for a subsequent volume. A round table discussion of this important subject has been proposed for the February meeting in 1933 and it is expected that additional papers will shortly become available.

Since the publication of the By-laws of the Division in the 1931 volume of the TRANSACTIONS, the number of standing committees has been increased (by letter ballot of the Division) from two to six; namely, Papers and Publications Committee, Finance Committee, Data Sheet Committee, Membership Committee, Annual Lecture Committee and Research Committee (if desirable) and the term of appointments in each case has been designated as three years, with approximately one-third of the committee membership to be appointed each year. In order to save space the revised By-laws are not printed in this volume, but it will be observed that the committees of the Division have been reorganized in conformity with the new regulations.

By authority of the Executive Committee and on the recommendation of the Secretary, Mr. W. M. Corse, the Chairman has appointed Mr. E. M. Wise to serve as Associate Secretary during the present year.

As in former years, the members are especially indebted to the Chairman of the Papers and Publications Committee of the Division, Mr. J. L. Christie, and the Chairman of the Data Sheet Committee, Mr. R. S. Archer, who have painstakingly supervised the major activity of the Division; its continuous program of presenting scientific and technical information in the form of Data Sheets (approximately 300 pages issued to date), TECHNICAL PUBLICATIONS, PREPRINTS and volumes of TRANSACTIONS. The interest and support of the membership at large constitute an appreciation of this service.

C. H. MATHEWSON, *Chairman*,  
Institute of Metals Division.

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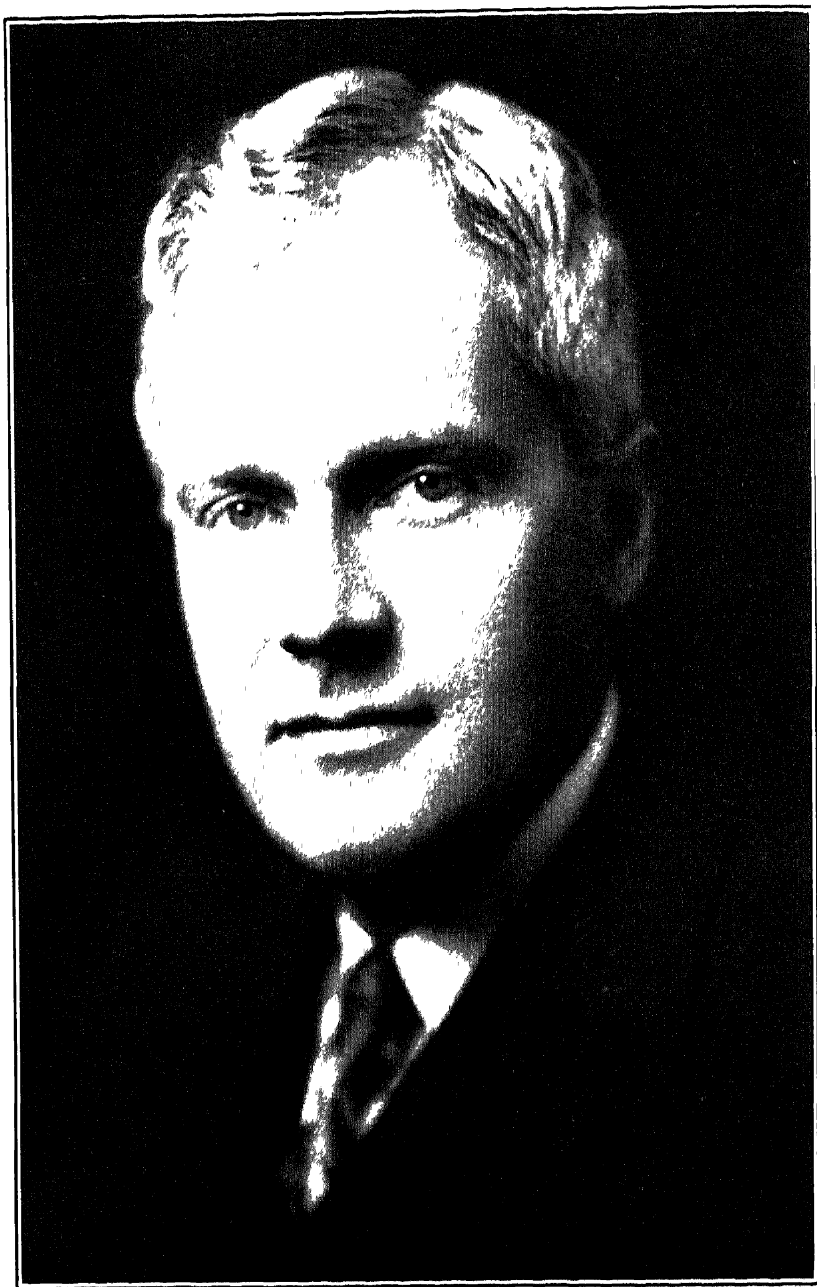
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PAUL D. MERICA  
*Institute of Metals Division Lecturer, 1932*

## The Age-hardening of Metals

BY PAUL D. MERICA,\* NEW YORK, N. Y.

(Institute of Metals Division Lecture, †)

WITHIN recent years it has become evident that the metallurgist's power to improve the properties of metals by heat treatment is far greater than it was formerly supposed to be. Although a few alloys were early known which respond favorably to heat treatment, notably steel, it was generally considered that the mechanical properties of most metals and alloys could be favorably altered only by mechanical working and annealing, operations of limited applicability only. The few isolated cases which were known of alloys hardenable by thermal treatment alone were deemed to be the metallurgical gifts of good fortune.

Today, in consequence of our better understanding of the phenomenon generally known as "age-hardening," we are familiar with many alloys which are hardenable by heat treatment alone, including those of all the common ductile metals. In fact, it is possibly not an exaggeration to say, quite contrary to our older conception, that hardenable alloys may be the rule rather than the exception among alloy systems.

One group of such alloys is susceptible to heat treatment in consequence of the fact that the alloys undergo transformations in the solid state. We are today able to utilize such transformations in the operation of age-hardening but we are not able to produce them at will in any desired alloy. Such alloys remain still the gifts of fortune!

On the other hand, there is a much larger group of alloy systems, hardenable by heat treatment, over which today the metallurgist may fairly be said to exercise some degree of domination. It is that group which is subject to what has rather loosely been called "dispersion-hardening," "precipitation-hardening" or sometimes merely "age-hardening" and which might more generally be called "supersaturated-solid-solution hardening."<sup>1</sup>

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\* Assistant to the President, The International Nickel Co., Inc.

† Presented at the New York Meeting, February, 1932. Eleventh annual lecture.

<sup>1</sup> It is unfortunate that there are no satisfactory names for these phenomena. Each of those mentioned lacks definiteness and some have possibly incorrect implications. I shall use the term "age-hardening" as the generic one, without theoretical or structural implications; the terms "dispersion-" and "precipitation-" hardening will be employed somewhat loosely, as is current usage, to describe the type of age-hardening occurring in the supersaturated-solution type of alloy. Whenever it is



Age-hardening of this sort occurs only in alloys of the solid solution type, of which the structural and phase relations are now fairly well understood. The alloy must contain a hardening constituent, be it metal or metallic compound, of which the solubility in the base alloy at higher temperatures is greater than at lower ones. The solid solution, saturated at higher temperatures with respect to the hardening constituent and rapidly cooled or quenched to lower ones is, at these temperatures, supersaturated and unstable. During the process of decomposition of this unstable solution, occurring gradually at lower or intermediate temperatures, the alloy age-hardens.

Now the significance of these supersaturated-solution-hardening systems lies, first of all, in the fact of their evident prevalence. Solid solutions and solid solubility are very common among alloy systems, and in them decreasing solubility with decreasing temperature is the rule. Alloy solid solutions may therefore be expected usually to have these orthodox solubility relations and consequently to exhibit the age-hardening phenomena which are found normally associated with them.

But even more significant is the fact that, understanding the nature and possibilities of alloy systems of this common type, we have it reasonably within our power to render any alloy composition amenable to age-hardening by the addition to it of a small amount of some suitably chosen hardening metal or metallic compound. We may perhaps fairly say that, theoretically at least, we are today in a position to harden any metal or alloy we please, and in that sense the metallurgist begins to exercise some systematic control over the mechanical properties of metallic materials.

It is of course that sort of domination over his materials which the metallurgist is ever seeking. He is striving to emulate the builder and the engineer in the flexibility of performance and the diversity of form of his creations. Unfortunately he has found his building materials—atoms—most stubborn and inflexible, and in consequence he has been obliged to discover rather than to design alloys. In this new-found ability to alter systematically and universally the values of one important set of properties in any alloy, we may see one of the directions in which progress is being made in the rational art of alloy building.

### AGE-HARDENING SYSTEMS

That our mastery of the art of age-hardening has been making rapid advances in recent years will be evident from the facts of Tables 1 and 2. All of the common ductile metals and most of the more common industrial

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desired to emphasize the somewhat formal difference between the two, I shall refer to "age-hardening" of the suppressed-transformation type and of the supersaturated-solution type.

alloys, including the austenitic steels, may be rendered susceptible to age-hardening by the addition of, usually, moderate quantities of some suitable hardening agent, and frequently several such agents are known for each metal or alloy. Many of these alloys are in industrial use today. When so "dosed" these metals or alloys may be structurally so modified by appropriate heat treatment as to exhibit increases in the values of their hardness and strength of 10 to 100 per cent, and even more.

The hardness of copper may thus be increased from its value of 35 Brinell in the annealed condition to about 400 in the 2.50 per cent beryllium-copper alloy. The tensile strength of 30 per cent copper-nickel alloys may be increased from 75,000 lb. per sq. in. to approximately 175,000 lb. per sq. in. in the 4 per cent aluminum-copper-nickel system. In the less generally known field of precious metals, none of which has a tensile strength over about 35,000 lb. per sq. in. in the annealed condition, tensile strengths of 175,000 to 200,000 lb. per sq. in. may be developed.

In short, strength and hardness values may be developed in many nonferrous alloys comparable with those of heat-treated steel, and age-hardening alloys are known which develop hardness values equal to those of the hardest steels known. In spite of the fact that this method of hardening metals is still quite in its infancy, the results of its application have so far been quite impressive, both in the extent of its applicability to alloy systems and in the actual physical results obtained by it in the various age-hardening alloys known today.

#### MECHANISM OF AGE-HARDENING IN SUPERSATURATED SOLID SOLUTIONS

Before continuing the discussion of the general aspects of age-hardening alloys, I should like to divert your attention for a moment to the nature of the mechanism of age-hardening. For the results of important researches carried out within the past decade, particularly on the Continent, have raised some question as to whether the simple theory of "dispersion-hardening" as originally proposed by Merica, Waltenberg and Scott<sup>(1)\*</sup> is adequate to explain all of the physical phenomena observed during the hardening process. Much of this recent research and discussion, although centering upon the age-hardening of duralumin, is nevertheless pertinent to and typical of dispersion-hardening systems generally, and it well merits our closest attention.

The four principal features of the original duralumin theory were these: (1) age-hardening is possible because of the solubility-temperature relation of the hardening constituent in aluminum, (2) the hardening constituent is  $\text{CuAl}_2$ , (3) hardening is caused by the precipitation of this constituent in some form other than that of atomic dispersion, and

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\* Superior figures in parentheses refer to bibliography at end of paper.

TABLE 1.—*Metals Hardened by Dispersion*

Metal	Hardening Element	Hardening Agent	Solubility				References	
			High		Low			
			Wt Per Cent	Temp, Deg C	Wt. Per Cent	Temp, Deg C		
Aluminum	Be	Be	0.1	645	0.05	600	1	
	Cu	CuAl <sub>2</sub>	5.65	548 E	0.5	200	2	
	Mg	β (SS)	14.9	451 E	4	200	3	
	Si	Si (+Al in SS)	1.5	570	0.4	RT	4	
	Ag	γ(SS)	48	558	0.75	200	5	
	Zn	γ(SS Al in Zn)	13.4	250	2.7	RT	4	
	Cu + 0.5 Mg	CuAl <sub>2</sub>	5.0	535 E	0.2	200	6	
	Mg <sub>2</sub> Si	Mg <sub>2</sub> Si	1.85	595 E	0.27	200	7	
	Cu + 0.84 Mg	Mg <sub>2</sub> Si +	3.1 Cu	530	< 0.4	400	6	
	+ 0.58 Si	Al-Cu-Mg-Si						
	Cu + 0.84 Mg	Mg <sub>2</sub> Si + CuAl <sub>2</sub>	4.7 Cu	515 E	< 0.8	300	6	
	+ 0.58 Si	+ Al-Cu-Mg-Si						
	Cobalt	Be	CoBe					8
		Al	β inversion					9
	Copper	Be	γ(SS)	2.4	800	0.75	400	8
		Cr	Cr(or CrCu SS)	0.8	1000	0.05-0.1	500	10
		Co	Co(or CoCu SS)	3.4	1000	0.35	RT	10
		Fe	Fe(+Cu in SS)	3.5	1050	0.2	RT	8
	Pd	Cu <sub>2</sub> Pd	100	555	16.7	400	11	
	Pt	Cu <sub>2</sub> Pt					12	
	Si	Cu <sub>2</sub> Si	6.8	800	< 2	RT	10	
	Ag	Ag(+Cu in SS)	2.3	779	0.00	RT	13	
	Ti		4-4.5	878	0.4	RT	14	
	Zn	β inversion	40-54	800	47-49	200	15	
	Be + P						16	
	Zn + Ni <sub>2</sub> Si						57	
	Be <sub>2</sub> Si	Be <sub>2</sub> Si					17	
	Co <sub>2</sub> Si	Co <sub>2</sub> Si + Co	3.3	1000	0.3	300	10	
		or Si						
	Cr <sub>2</sub> Si	Cr <sub>2</sub> Si					10	
	Mn <sub>2</sub> Si	Mn <sub>2</sub> Si					17	
	Ni + Al						18	
	Ni <sub>2</sub> Si	Ni <sub>2</sub> Si	8.2	1000	0.7	300	10	
	Ni + Sn						19 & 20	
	Sn + Ni <sub>2</sub> Si						57	
	Ni + P	Ni <sub>3</sub> P					21	
	Sn + P + Ni <sub>2</sub> Si						57	
Gold.....	Cu	AuCu	100	520	12	RT	22	
		Suppressed Change						
	Fe	AuFe <sub>3</sub>	36	1180	10	400	12	
	Pt	β(PtAu + Au)	100	1150	20	600	23	
	Ni <sub>2</sub> Si	Ni <sub>2</sub> Si					24	
	Co <sub>2</sub> Si	Co <sub>2</sub> Si					24	
	Cr <sub>2</sub> Si	Cr <sub>2</sub> Si					24	
	Ni	Ni + (Au SS)	40	830	8	600-300	25	
	Ni + Al						12	
	Ni + Zn						26	
	Ag + Cu						27	
	Pd + Zn						12	
	Pt + Zn						12	
	Iron .....	Be						28
		C	Fe <sub>3</sub> C	0.04	710 E	0.006	RT	29
		Cu	Cu(+Fe SS)	3.4	810 E	0.4	600-RT	30
		Mo	Mo or Fe <sub>2</sub> Mo <sub>3</sub>	24	1440	6	400	31
		N	Fe <sub>2</sub> N	0.5	580 E	0.01	RT	32

TABLE 1.—(Continued)

Metal	Hardening Element	Hardening Agent	Solubility				References
			High		Low		
			Wt. Per Cent	Temp. Deg. C.	Wt. Per Cent	Temp. Deg. C.	
Lead .	O	FeO	0.10	715	0.035-0.05	RT	33 34
	W	Fe <sub>3</sub> W <sub>2</sub>	33	1525 E	8	RT	35
	Cr + Ni + B	"					52
	Ni + Ti						36
	Ni + Mn + Mo						37
	Ni + Ti + Cr						36
	Ni + Mn + Co + Ti						53
	Ti + Mn + Ni	Fe <sub>3</sub> Ti	6.3	1300			37
	Sb	Sb	2.45	247 E	0.80	RT	38
	Sb + Cd						54
	Sb + Cu	Compd					38
	Sb + Ag	With Sb					38
	Sb + Mn	With Sb					38
	Sb + As	With Sb					38
Magnesium..	Cd + Sn						54
	Ca	Pb <sub>2</sub> Ca	0.1	328 P	0.01	RT	39
	Al	Mg <sub>2</sub> Al <sub>3</sub>	12	435	< 6	RT	40
	Cd(Slight)						41
Molybdenum..	Zn	MgZn <sub>2</sub>	6	342 E	2	RT	41
	Sn(Slight)		3-4	E			41
Nickel..	Fe	Fe <sub>3</sub> Mo <sub>2</sub>	11	1540	5	RT	31
	Be	NiBe(compd)	2	1140			8
Monel.....	Mg				<0.1	500	61
	Mg + C				<0.1	500	61
	Al						42
	Ti						42
Palladium .	Si		4.1	900	3.1	600	43
	Cu	PdCu		Suppressed change	37 to 50 per cent Cu, 670° to 620° C.		11
Platinum...	Cu + Ag	PdCu?					27
	Cu + Au + Ag	AuCu + PdCu?					27
	Cu	PtCu		Suppressed change			12
	Au	β (SS)	100	1150	5	600	23
Silver... ..	Ag + Au + Cu						27
	Fe?						
	Cu	Cu(+Ag in SS)	8.9	799	0.94	RT	13
	Cu + Al	CuAl <sub>3</sub>					17
	Cd	γ (SS)					44
	Cu + Cd	Cu <sub>2</sub> Cd					12
	Pd + Cu						27
	Si						24
Tin.....	Si + Cu	Cu <sub>2</sub> Si					24
	Zn	β inversion					44
	(92Ag 5 7 5 Zn) + Cu		7	700	< 1	280	45
	Cu + Mg	Cu <sub>2</sub> Mg ?					17
	Cu + Sb	Cu <sub>2</sub> Sb ?					17
	Mg + Zn	MgZn <sub>2</sub> ?					17
	Cd + Sb	CdSb ?					17
	7 % Sb + 2 % Cu						55
Zinc.....	Al	Al + (Zn in SS)		β Inversion			8
	Cd	Cd + (Zn in SS)	3.7	263 E	0.92	142	46
	Cu + Ag						56

probably in fine disperse molecular, colloidal or crystalline form, and (4) the hardening effect of  $\text{CuAl}_2$  in aluminum was deemed to be related to its particle size in the manner indicated by the graph in Fig. 1.

The optimum effect upon the hardness of aluminum was considered to be exerted when the  $\text{CuAl}_2$  was critically dispersed in the form of particles having an average linear size lying somewhere between that of atoms and that of about  $10^{-5}$  cm. According to this theory, hardening is due to the increasing hardening effectiveness of particles of size greater than atoms, whereas subsequent softening is due to the decrease in the number of hardening particles available, as their size increases.

TABLE 2.—*Physical Properties of Age-hardenable Metals*

Metal or Alloy	Annealed Metal or Quenched Alloy			Cold-worked Metal or Aged Alloy			References
	Brinell Hardness	Tensile Strength, Lb. per Sq. in.	Elongation, Per Cent	Brinell Hardness	Tensile Strength, Lb. per Sq. in.	Elongation, Per Cent	
Aluminum.....	25	13,750	40	38	24,000	10	47
Aluminum + 4 % Cu.....	65	38,000	6	100	50,000	1	48
Copper.....	40	33,000	60	100	65,000	5	49
Copper + 2.75 % Be ..	116	88,000	29	365	161,000	5	58
Copper + 6 % Ni <sub>3</sub> Si.....	68	47,000	55	204	115,000	16	10
42.6 % Gold + 28.1 % Pt + 15.5 % Ag + 13.3 % Cu + 0.5 % Zn.....		135,000	15		179,000	0.34	27
Lead.....	4	2,800		8			54, 60
Lead + 0.085 % Ca.....		3,800			7,400		39
Iron.....	75	40,000	50	150	80,000	5	49
Steel (0.57 C).....	185	95,000	25	580	215,000	0	59
Iron + 12 % Mo.....	155	58,200	6	230	147,000	1	31
Nickel.....	100	65,000	50	175	135,000	5	49
Nickel + 2.5 % Be.....	175	80,000	17	500	150,000	2	50
Copper-nickel (67 % Ni).....	130	75,000	50	200	150,000	5	49
Copper-nickel + 4 % Al.....	140	90,000	50	300	175,000	20	51

There appears to be no question but that the atomic changes which occur during hardening, and which therefore may be said to cause it, are the direct result of the instability of a supersaturated solid solution and of its gradual decomposition in some manner during aging. And it is highly probable that the degree of dispersion of the hardening element in the fully hardened alloy is something less than atomic dispersion.

It has likewise been confirmed subsequently that all of the phenomena of age-hardening in duralumin, whether at room temperatures or higher ones, are fully reproduced in a pure 5 per cent copper-aluminum alloy

free from magnesium, silicon and iron,<sup>2</sup> although copper-free magnesium-silicon-aluminum alloys will also age-harden as Hanson and Gayler<sup>(2)</sup> have shown, due probably but not certainly<sup>3</sup> to the precipitation of  $Mg_2Si$ .

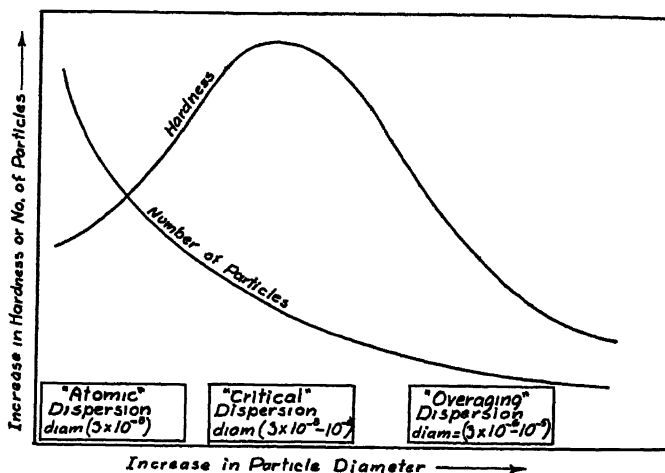


FIG. 1.—SIMPLE CONCEPTION OF EFFECT OF PARTICLE SIZE AND NUMBER ON HARDENING POWER OF A CONSTANT AMOUNT OF HARDENING CONSTITUENT.

The aspect of the duralumin problem which at present is principally in doubt is that of the nature of the decomposition which occurs in the saturated solution during aging, and particularly the question whether precipitation in the usual sense actually then occurs or not.

#### OBJECTIONS TO THE SIMPLE THEORY

Fraenkel<sup>(3,4,5,6)</sup> was the first to raise objection to the simple "dispersion" theory, calling attention to his discovery that, although the electrical resistivity of duralumin decreases during aging at higher temperatures (100° to 250° C.), it actually increases during aging at ordinary temperatures. It was not in accord with our simple knowledge of the electrical properties of solid solutions that their resistivity should increase with decreasing concentration.

He was the first to suggest the possibility that the mechanism of age-hardening at room temperatures might be essentially different from that at higher ones (150° to 250° C.) and that it might be homogeneous in nature; namely, that the hardening reaction might occur wholly within the single phase—aluminum solid solution—and without any precipitation of a second phase. We shall see that his ideas subsequently received further experimental confirmation and have found other adherents.

<sup>2</sup> The extent of hardening at room temperatures, however, is substantially less in pure copper-aluminum alloy than in duralumin.

<sup>3</sup> In the subsequent remarks  $Mg_2Si$ , for convenience of expression, will be assumed to be the actual hardening constituent in the magnesium-silicon-aluminum system.

## ABSENCE OF DIRECT PROOF OF PRECIPITATION

Although Dix and Richardson<sup>(7)</sup> were able to secure visual microscopic evidence of the precipitation of  $\text{CuAl}_2$  in copper-aluminum alloy aged at temperatures of  $200^\circ \text{C}$ . and above, it has never been possible to demonstrate the precipitation of  $\text{CuAl}_2$  or of  $\text{Mg}_2\text{Si}$  in duralumin aged at lower temperatures, at which nevertheless such alloys may be fully hardened. This was at first explained as being due to the failure of the microscope to permit resolution of particles smaller than about  $10^{-5}$  cm. in diameter, which might nevertheless be 1000 times larger than atoms.

Schmid and Wassermann<sup>(8)</sup> with the much more sensitive X-ray spectrograph were able to identify the characteristic lines of crystalline  $\text{CuAl}_2$  in the diffraction photographs of annealed duralumin, but were unable to find them in fully hardened duralumin, even when aged at temperatures between  $150^\circ$  and  $200^\circ \text{C}$ . They were likewise unable to find  $\text{Mg}_2\text{Si}$  lines even in annealed duralumin, but considered their evidence inconclusive on this point.

However, we may not accept even this negative result as conclusive, since, as Schmid and Wassermann themselves warned, the lines resulting

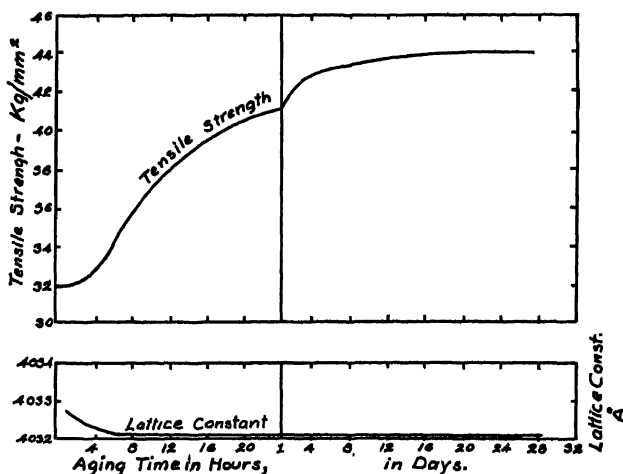


FIG. 2.—LATTICE CONSTANT AND TENSILE STRENGTH DURING ROOM-TEMPERATURE AGING OF QUENCHED DURALUMIN (Schmid and Wassermann<sup>(8)</sup>).

from the diffraction of X-rays by very small crystalline particles broaden rapidly and become ill-resolved at particle diameters less than about  $10^{-6}$  cm. If well defined  $\text{CuAl}_2$  or  $\text{Mg}_2\text{Si}$  crystals could and do actually exist in hardened duralumin, having particle diameters less than about 10 times the average atom diameter, they might escape detection by X-ray analysis.

But there is further and more revelatory X-ray evidence on this question of precipitation. When copper is taken up by aluminum in solid solution, the lattice constant of aluminum is continuously decreased, the change being almost proportional to the amount of copper

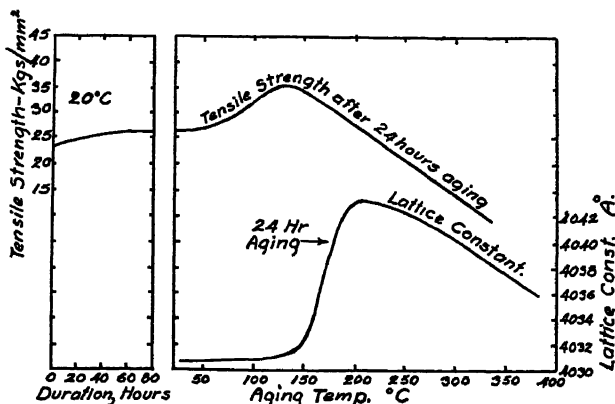


FIG. 3.—LATTICE CONSTANT AND TENSILE STRENGTH DURING AGING OF QUENCHED 5 PER CENT COPPER-ALUMINUM ALLOY (Göler and Sachs<sup>(10)</sup>).

in solid solution.<sup>(9)</sup> Schmid and Wassermann<sup>(9)</sup> and others<sup>(10,11)</sup> were able to show that the lattice constant of quenched supersaturated duralumin remains unaltered during aging treatments at room tem-

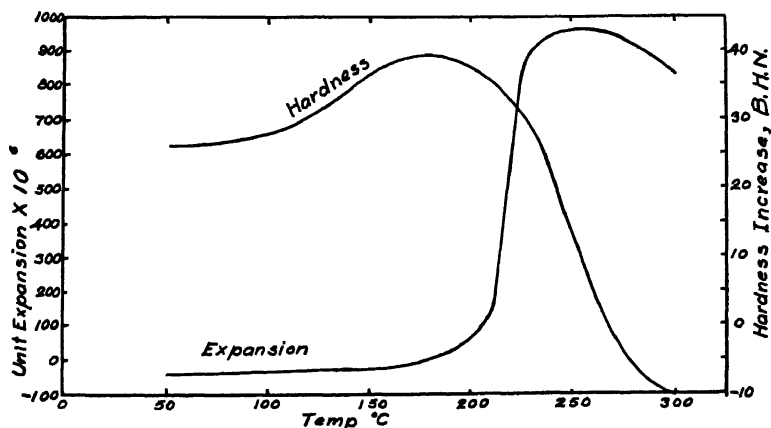


FIG. 4.—LINEAR EXPANSION AND HARDNESS AFTER 8 HR. AGING AT DIFFERENT TEMPERATURES OF 4.30 PER CENT COPPER-ALUMINUM ALLOY (Portevin and Chevenard<sup>(12)</sup>).

perature, and even at higher temperatures up to 150° C., during which substantial hardening takes place. It reverts to the value for pure aluminum only after tempering at higher temperatures, at which some over-aging and softening occurs. These interesting facts are shown graphically



in Figs. 2 and 3. They suggest that the hardening components, copper, magnesium and silicon, may still be in solid solution in the fully hardened condition.

Further confirmatory evidence with respect to the absence of precipitation is yielded by the dilatometric studies by Kikuta,<sup>(12)</sup> Portevin and

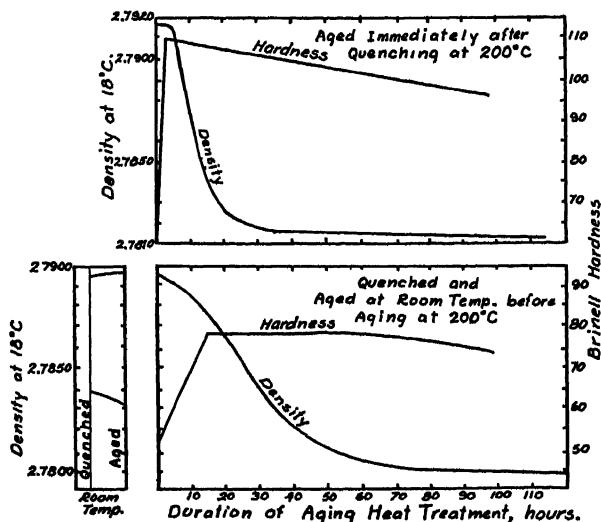


FIG. 5.—DENSITY AND HARDNESS DURING AGING AT 200° C. OF 4.50 PER CENT COPPER-ALUMINUM ALLOY (Gaylor and Preston<sup>(11)</sup>).

Chevenard<sup>(13)</sup> and others<sup>(11)</sup> who found, as shown in Figs. 4 and 5, that at room temperatures and even above, pure copper-aluminum alloy

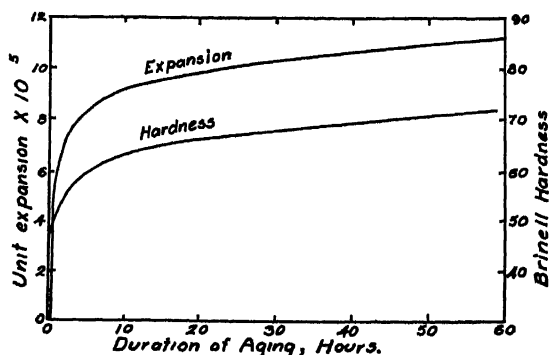


FIG. 6.—LINEAR EXPANSION AND HARDNESS DURING ROOM-TEMPERATURE AGING OF MAGNESIUM-SILICON-ALUMINUM ALLOY (Portevin and Chevenard<sup>(13)</sup>).

hardened during aging without appreciable increase in specific volume, and that only during age-hardening at temperatures above about 200° C. did the specific volume increase, as it should, were CuAl<sub>3</sub> precipitating from solid solution. On the other hand, as shown in Fig. 6, a copper-

free, magnesium-silicon-aluminum alloy behaved quite normally; its specific volume and its hardness increased together during aging, as should be the case if  $Mg_2Si$  were being precipitated during the hardening process.<sup>4</sup>

#### PRESENT STATUS OF THE "PRECIPITATION-HARDENING" THEORY

Our picture of the mechanism of age-hardening in duralumin must, therefore, differ in some respects in 1932 from that in 1919. There can be no question, in view of the evidence just described, that at higher temperatures age-hardening of copper-aluminum alloy is accompanied by the actual precipitation of crystalline particles of  $CuAl_2$  in fine dispersion, and that therefore age-hardening can and does occur in aluminum alloys substantially in accordance with the simple views originally proposed. Similarly it appears probable that even at room temperature age-hardening of magnesium-silicon-aluminum alloy is accompanied by the precipitation of some separate phase, probably  $Mg_2Si$ , but there may be some doubt as to whether this precipitate is of wholly crystalline character.

On the other hand, the evidence appears to me very convincing that during the age-hardening of copper-aluminum alloy at temperatures below 150° C. no precipitation in the ordinary sense takes place, of discrete, crystalline particles of  $CuAl_2$ . At these temperatures hardening is substantially completed before any such precipitation occurs, and I think we must accept the conclusion that age-hardening in this alloy and in super-saturated-solution alloys generally *may also occur in consequence of some structural alteration other than that of the precipitation of excess solute.*

#### OTHER MECHANISMS OF AGE-HARDENING

What then is the nature of the alteration in duralumin which causes age-hardening at room temperatures? Is it essentially different from, or is it similar to, the simple mechanism of age-hardening at higher temperatures? I do not believe that our present evidence permits definite answers to these questions. We shall have to be content for the moment with seeking the most probable ones—and in so doing to rely often upon arguments of general and indirect character.

#### DIFFUSION PROBABLY DOES OCCUR DURING ROOM-TEMPERATURE AGING OF DURALUMIN

Age-hardening, whatever its mechanism, develops only gradually and requires time for its consummation. At high temperatures this time is

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<sup>4</sup> The dilatometric method appears to be a very effective and elegant one in studying age-hardening processes, and it should be possible by its aid to answer the question finally as to the identity of the constituent which causes room-temperature hardening in duralumin, whether  $CuAl_2$  or  $Mg_2Si$ .

certainly principally required for the diffusion of copper atoms. Diffusion of magnesium and of silicon atoms is likewise required for the formation and precipitation of  $\text{Mg}_2\text{Si}$  during the room-temperature aging of magnesium-silicon-aluminum alloy. It is natural to assume that diffusion and segregation of copper atoms also take place during room-temperature aging, and Hengstenberg and Wassermann<sup>(14)</sup> have indeed found some evidence of this in the increasing intensity of the X-ray line spectra and the decreasing intensity of diffuse radiation during room-temperature aging of copper-aluminum alloy.

If such diffusion does not take place, it is most difficult to imagine an alternative atomic rearrangement which could cause hardening and which would also require time for its completion. The formation of a simple unpolymerized molecule of  $\text{CuAl}_2$  might harden the aluminum lattice; but one would expect that such a rearrangement could occur almost instantaneously, even if associated with some rotation of the molecule in, or distortion of, the surrounding lattice.<sup>5</sup>

Although our available data yield no final and conclusive answer in this respect, I regard the assumption as reasonably well justified that diffusion does occur and that it plays an important role in the room-temperature age-hardening of duralumin just as it does in its age-hardening at higher temperatures.

Whither then do the copper atoms diffuse? They must, of course, diffuse in such a manner as to segregate in groups—but there are several types of groups which might thus be formed. The most natural assumption is that they diffuse toward, or to, positions which they would occupy just prior to atomic rearrangement and precipitation as crystalline particles of  $\text{CuAl}_2$ .

They might, however, diffuse toward or to, other positions. Thus they might arrange themselves preferentially along certain lattice planes, constituting a sort of interpenetrating lattice, according to the view held by Tammann.<sup>(15)</sup> They might diffuse toward, or to, positions which they would occupy on the lattice of some compound other than  $\text{CuAl}_2$ —an intermediate, metastable compound or molecule presumably of high aluminum content, a possibility contemplated, apparently, by some students of age-hardening.<sup>(3,4)</sup>

Now, although there exists no evidence in direct support of these and other alternative possibilities, neither can they be denied with assurance. The balance of present evidence, however, appears to favor the simple and natural hypothesis that diffusion of copper atoms at room temperature takes place in such a manner as to prepare for their actual precipitation as

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<sup>5</sup> It is conceivable, however, that a metastable or pseudomolecule containing only one copper atom but many aluminum atoms might be formed only gradually; such a molecule, of course, might very effectively harden the matrix also.

crystalline  $\text{CuAl}_2$  particles. They assemble in random groups on lattice positions of the duralumin, not of the  $\text{CuAl}_2$  lattice. This hypothesis is supported indirectly by the fact that, as shown in Fig. 5, age-hardening of copper-aluminum alloy even at  $200^\circ \text{C}$ . is practically completed before precipitation of  $\text{CuAl}_2$  takes place, suggesting that the same preparation, by way of diffusion, is made for precipitation at  $200^\circ \text{C}$ . as at room temperature. It is the view held by several prominent investigators of the duralumin problem, including particularly Jeffries and Archer,<sup>(18)</sup> Gayler and Preston,<sup>(11)</sup> and Honda;<sup>(21)</sup> it is not irreconcilable with the views of Fraenkel.

#### AGE-HARDENING BY DISTORTED GROUPS OR "KNOTS" OF HARDENING ATOMS

We may picture these groups, or lattice regions so formed by diffusion, as having local concentrations of copper atoms equal to or less than that required for the formation of a  $\text{CuAl}_2$  lattice; their concentration might vary, however, from center to periphery of the groups. The latter will vary in size and shape, but must contain at least two atoms of copper and possibly, as Guertler<sup>(17)</sup> has suggested, not as many as are required to form a crystalline nucleus, which might be the unit cell, requiring in the case of  $\text{CuAl}_2$ , four copper atoms.<sup>(19)</sup> These groups are not separated from the surrounding aluminum lattice by an interface. Fig. 7 represents an attempt to illustrate diagrammatically the nature of such groups.

In consequence of the local crowded presence of copper atoms on a lattice which will not hold them in equilibrium, this lattice must be much distorted and contracted throughout and adjacent to these small regions, and in fact it may not be proper to regard these as wholly crystalline. The atomic arrangements in different groups probably represent different degrees of transition from the lattice of aluminum to that of  $\text{CuAl}_2$ , these variations being determined by a multitude of internal factors.

These groups or "knots," if I may so call them, in the aluminum lattice, are sufficiently distorted and "rough" in atomic structure to resist slip and deformation fairly efficiently. They are, in other words, effectively "hard" and may be considered to act, as far as deformation in the surrounding aluminum lattice is concerned, substantially as crystalline particles of  $\text{CuAl}_2$  would act could they be formed in the same locations, with the same approximate orientation, and in similar sizes and shapes.

Here then is that modification of the simple dispersion-hardening theory which appears justified by our present knowledge of this phenomenon. Not only can finely dispersed crystalline particles of a precipitated phase harden a metallic matrix, as they indeed do during the high-temperature aging of duralumin and in other cases, but hardening can similarly be effected by a finely dispersed group of such "knots" or "pseudo particles"—particles about to be born. And such hardening can

likewise be effected by particles in any transition states between these two. In duralumin, aged at room temperature, and in some other cases, it is not the crystalline particles themselves, but their "embryos," which actually occasion age-hardening.

We may thus picture the mechanism of hardening by "knots" in accordance with the well-known "slip-interference" theory of Jeffries and Archer,<sup>(18)</sup> substantially in the same manner as in the case of alloys in which the dispersed particles are discrete and crystalline.

#### SOME OBSCURE ASPECTS OF AGE-HARDENING

This structural picture of "homogeneous" age-hardening reactions appears to fit the known facts better than any other and it presents no difficulties not shared by other theories; nevertheless it must be accepted provisionally and subject to confirmation or correction in the light of further experimental data. There are, indeed, still some aspects of the phenomenon of aging of which the precise interpretation remains obscure.

*Lattice Distortion.*—One of these aspects is the question of internal distortion during age-hardening. Rosenhain<sup>(20)</sup> and Honda<sup>(21)</sup> have pointed out the significance of lattice distortion in obstructing internal slip, and it is this feature of age-hardening, also, which is emphasized in the "pseudomolecule" hardening theory of Dean and Gregg.<sup>(16)</sup> Indeed, by some, paramount importance has been ascribed to lattice distortion, in explaining age-hardening.

In connection with lattice "knots" such as have been postulated, lattice distortion must be of great importance, since it is to such distortion, whether contraction or expansion, within the lattice region forming the "knot," that its power of obstructing slip is wholly due. Even with dispersed crystalline particles, the lattice immediately surrounding them must be distorted by their presence, and the effective size of the particle is increased thereby in obstructing and diverting slip, as was pointed out some years ago;<sup>(22)</sup> this lattice distortion thus permits the optimum development of "slip interference."

In the 5 per cent copper-aluminum alloy, the "knots" presumably exhibit a reduced lattice spacing, reflecting the tendency of an assemblage of copper and aluminum atoms, in the right proportion, to form the contracted lattice of  $\text{CuAl}_2$ ; the latter having an atom density about 10 per cent less than that of the supersaturated solid solution. The distribution of atomic distances, therefore, within a fully age-hardened lattice containing such distorted "knots," must be quite different from that within the freshly quenched supersaturated solid solution. X-ray diffraction, however, yields no evidence of this distortion or of this difference. The diffraction lines are not only in the same position, indicating an unchanged average lattice constant, but they are practically as sharp in copper-

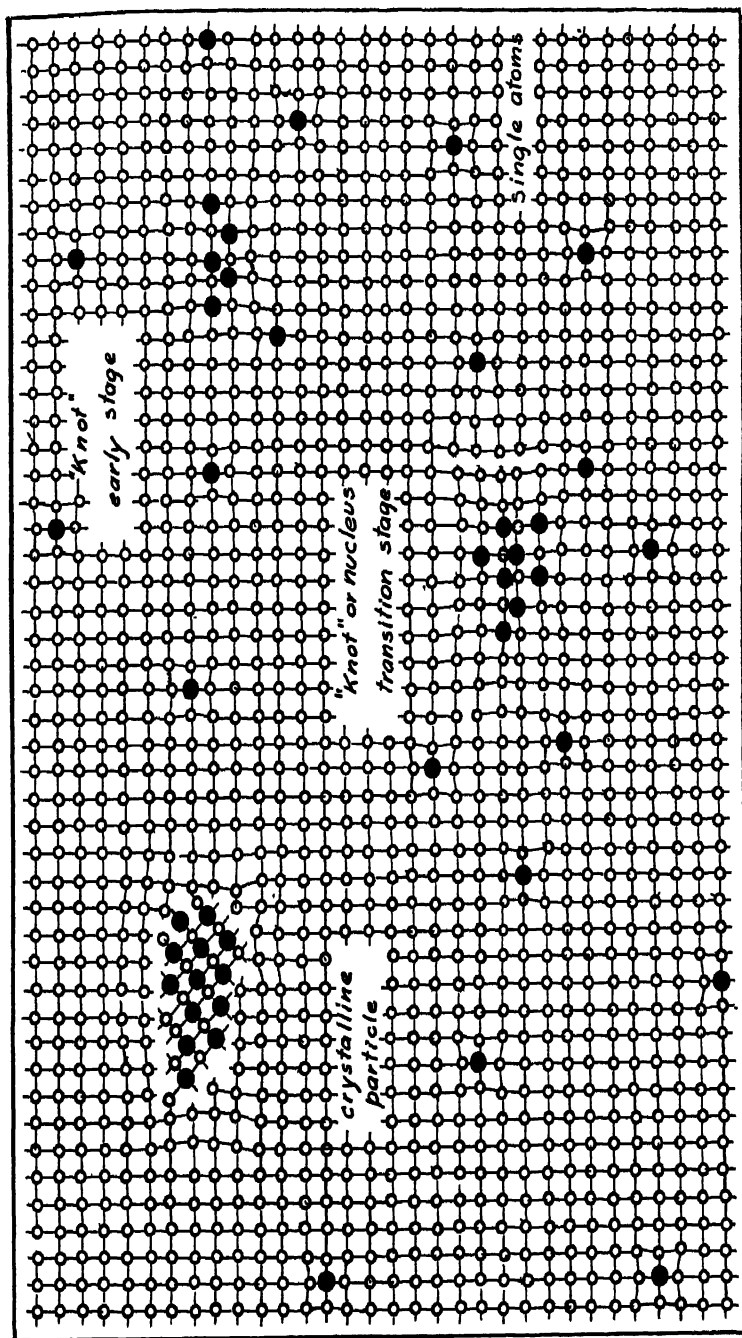


Fig. 7.—ILLUSTRATION OF SUPPOSED ATOMIC ARRANGEMENT IN "LATTICE KNOTS" AND IN CRYSTALLINE PARTICLES. Single atoms distort slightly the surrounding lattice. "Knots" in their early stages are small, and atom planes are continuous but considerably distorted. In intermediate or transition stages "knots" are larger and some disregistry of atom planes appears. Crystalline particles exhibit practically complete atom-plane disregistry except perhaps along one set of planes.

aluminum alloy fully aged at room temperature as in the same alloy freshly quenched.<sup>6</sup>

Only when  $\text{CuAl}_2$  is actually precipitating from the lattice during aging at  $200^\circ \text{C}$ . does diffuseness appear in the X-ray line spectra, and the specimen then diffracts as if there were regions within it which had been "released" by the migration and precipitation of the copper atoms, and which diffract the X-rays just as the lattice of pure aluminum.<sup>(11)</sup>

The X-ray evidence does not, therefore, appear to support the lattice "knot" hypothesis. We are not entitled, however, to accept it as in definite contradiction to the latter, since the X-ray method does not appear to be capable of indicating localized lattice distortion in certain types of distribution. This we know from experience with the X-ray spectra of solid solutions, which are practically as clear and sharp as those of pure metals, indicating that this method is in some respects a very tolerant integrator of the internal state of affairs in crystal lattices.

*Diffusion.*—The diffusion of copper atoms during room-temperature aging of copper-aluminum alloy also deserves a bit of attention. For we conceive of atomic diffusion as proceeding normally in the direction of lowered atomic concentration and in the direction of decreased lattice distortion. But the direction of this diffusion is just the reverse of what we deem normal; although quite spontaneous, it proceeds "up-hill," if you please. It is not, of course, unique in age-hardening processes, but it attracts our attention because of the relative stability of the concentrated "knots" formed thereby.<sup>7</sup>

What I want to emphasize is the fact that both "down-hill" and "up-hill" atomic diffusion may proceed during age-hardening, and possibly even simultaneously in any large lattice region. The stability of the end products of "up-hill" diffusion may be different in character from that of the products of the more normal "down-hill" diffusion and this fact may have an important bearing upon an aspect of precipitation-hardening which has attracted considerable attention; *viz.*, that of so-called "incubation."

*Incubation.*—Freshly quenched duralumin does not at room temperature begin to harden immediately, as can be seen from the graphical data of Fig. 2. An incubation period of variable duration intervenes before there is any mechanical evidence of alteration in the alloy. This period of incubation is characteristic of the age-hardening of duralumin at all

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<sup>6</sup> There has been some controversy on this question chiefly between Gayler and Preston<sup>(11)</sup> and Schmid and Wassermann<sup>(9)</sup> from which it would appear that even slight amounts of cold working will produce distortion effects (broadening of Debye-Scherrer lines) which appear to be absent in undeformed, room-temperature aged copper-aluminum alloys.

<sup>7</sup> It may be suggested that in one respect "up-hill" diffusion may differ from the normal variety; it may probably occur at lower temperatures than the other.

temperatures and has been noticed in other age-hardening alloys as well, by Masing,<sup>(26)</sup> Dean<sup>(23)</sup> and others.

During this initial period the atoms of the lattice are not entirely idle, however, since there are other physical indications of atomic activity; *viz.*, appreciable changes in electrical resistivity and in specific volume. Diffusion probably begins immediately in freshly quenched duralumin, but some time is required before enough atoms have traveled far enough to produce hardening segregation. The simple incubation period is not difficult to understand and, indeed, would be expected.

More difficult of comprehension, however, are the effects of aging at lower temperatures upon the chronology of hardening at higher aging temperatures, phenomena of which the importance has been often empha-

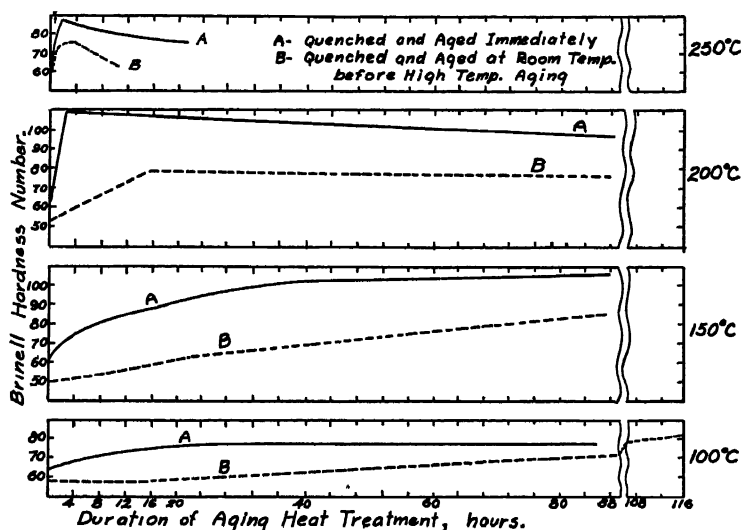


FIG. 8.—EFFECT OF PRIOR ROOM-TEMPERATURE AGING UPON THE COURSE OF AGE-HARDENING AT HIGHER TEMPERATURES OF 4.50 PER CENT COPPER-ALUMINUM ALLOY. (Gayler and Preston<sup>(11)</sup>).

The hardness of specimens aged immediately after quenching is shown by the full-drawn curves; that of specimens previously aged before similar treatment for 14 to 61 days at room temperature, by the dotted curves.

sized (Dean,<sup>(23)</sup> Gayler and Preston<sup>(11)</sup>). The facts are well illustrated in Figs. 8 and 9, wherein are compared the hardness-time curves during aging at higher temperatures of freshly quenched specimens and of specimens quenched and previously aged for considerable periods at room temperatures. It is evident that prior room-temperature aging not only delays the initiation of age-hardening at higher temperatures but influences the hardness values ultimately attained during subsequent high-temperature aging. This is true not only of alloys which harden during such prior aging but also of alloys which do not. The hardness often



lattice "knot" theory of hardening in cases in which precipitation does not occur.

In the 2.5 per cent beryllium-copper alloy, for example, we have no reason to suspect the intervention of any other reaction during age-hardening than that of the actual precipitation of the beta hardening compound. Yet age-hardening is accompanied by the same sort of incubation phenomena as are encountered in the duralumin system. The time rates of hardening also display certain irregularities, often of seeming rhythmic character, which emphasize the local nature of the hardening mechanism and suggest the unstable nature of the equilibrium conditions which are initially attained.<sup>(26)</sup>

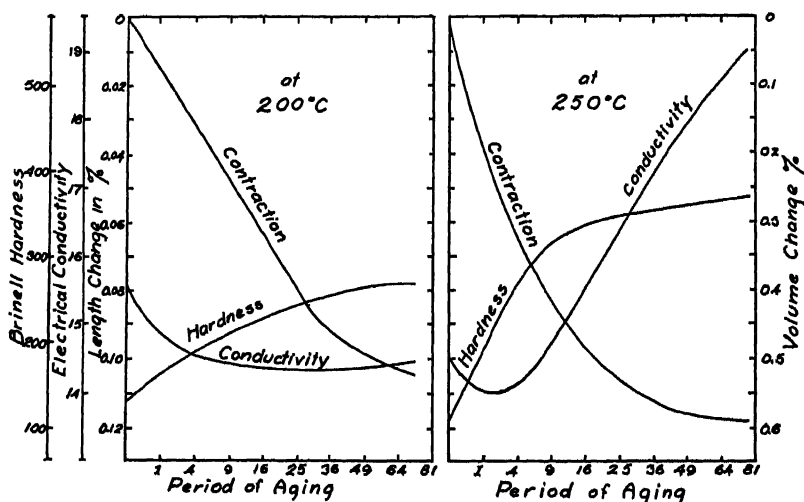


FIG. 10.—HARDNESS, CONTRACTION AND ELECTRICAL CONDUCTIVITY DURING AGING OF QUENCHED 2.5 PER CENT BERYLLIUM-COPPER ALLOY (*Masing and Dahl*<sup>(26)</sup>).

Furthermore, as shown in Fig. 10, the electrical conductivity shows the characteristic abnormality of duralumin. At higher temperatures of aging (350° C. and over) it uniformly increases as it normally should. At 150° C. it decreases during aging. At intermediate aging temperatures it first falls temporarily, then rises steadily as hardening progresses.<sup>10</sup>

Age-hardening in the 8 per cent copper-silver alloy,<sup>(27)</sup> in so far as it has been studied, appears to proceed without any anomaly, even with respect to the electrical conductivity as shown in the data of Fig. 11, from which it is evident that hardening in this system is always accompanied by an increase of electrical conductivity, as might be expected from the simple "dispersion" theory. This appears to be true also of

<sup>10</sup> The electrical conductivity behaves similarly in other otherwise normal age-hardening alloys such as the titanium-nickel-manganese austenitic steels.<sup>(18)</sup>

the magnesium-copper alloys, which age-harden at all temperatures with increase of electrical conductivity.<sup>(64)</sup>

*Electrical Conductivity.*—The fact that the electrical conductivity may behave abnormally during the aging of alloys in which actual precipitation is under way, as well as in alloys of the duralumin type, requires us to seek an explanation for this anomaly, which is not peculiar to nonprecipitating age-hardening systems.<sup>11</sup>

Electrical conductivity is notoriously sensitive to a number of physical and structural factors involved in the process of age-hardening, and the value of the conductivity in any region within which age-hardening has occurred is the average of that of its various component portions and the resultant of the effects of these other complicating factors. The history of the variation of its value during the process of age-hardening

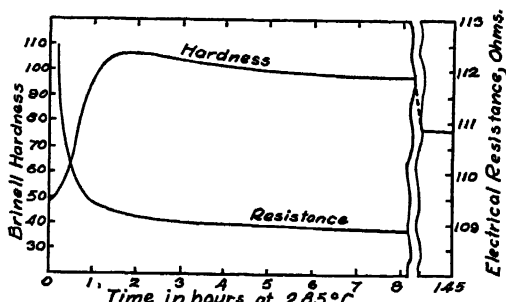


FIG. 11.—ELECTRICAL RESISTANCE AND HARDNESS DURING AGING OF QUENCHED COPPER-SILVER ALLOY (Fraenkel<sup>(21)</sup>).

is hardly susceptible, therefore, of any simple interpretation. The systems of internal stresses and of local lattice distortion, which are set up in any lattice by the segregation and the precipitation of the hardening constituent, must have an important effect upon the conductivity, and it seems that therein may be found the principal explanation for the curious irregularities encountered in its behavior.<sup>12</sup> If the presence of local internal stresses occasions the anomalous decrease in conductivity during low-temperature aging, it is not difficult to understand why this anomaly disappears at higher aging temperatures.

*Aluminum-copper-nickel System.*—Very pronounced age-hardening phenomena are exhibited by the copper-nickel alloys containing more than about 5 per cent of either copper or nickel, to which from 1 to 10 per cent of aluminum has been added. This has been demonstrated by

<sup>11</sup> Höjendahl<sup>(25)</sup> presents some interesting views, emphasizing the favorable effect upon conductivity of regularity of distribution of disturbances in any lattice.

<sup>12</sup> This aspect has been stressed by H. Essen and W. Eilender, who emphasize the effect upon conductivity of the "cold working" of the lattice occasioned by the precipitation of the hardening particles.

Read and Greaves<sup>(30)</sup> for the copper-rich alloys and by Mudge<sup>(31)</sup> for the nickel-rich and intermediate alloys. There is still uncertainty as to the identity of the constituent which causes hardening in these alloys, and indeed it is not clear whether the hardening constituent is the same in the copper-rich as it is in the other copper-nickel alloys. It seems likely from the work of Austin and Murphy,<sup>(32)</sup> however, that it is due to a solid solution of NiAl and Cu<sub>3</sub>Al in varying proportions.

In the copper-rich alloys containing less than 10 per cent of nickel, age-hardening is accompanied by the precipitation of this compound in particles of microscopically visible dimensions; nevertheless the induced hardening is considerable, comprising strength increases up to 50 per cent and hardness increases amounting to 100 per cent, and over.

These alloys illustrate the possibility of influencing the solubility-temperature relations in any given alloy by the addition of a third metal. According to Read and Greaves, the addition of from 5 to 10 per cent of nickel to an aluminum bronze diminishes the solubility of the Cu<sub>3</sub>Al compound at lower temperatures from about 10 to about 3 per cent aluminum, while not affecting it at the higher ones. The solubility of this compound in the absence of nickel is about 10 per cent at all temperatures, and the addition of nickel has therefore transformed a non-age-hardening into an age-hardening alloy, by its simple effect on the solubility relations within the base alloy. This effect of nickel undoubtedly is due in part to its combination with the hardening constituent itself.<sup>13</sup>

Within the range of alloys containing from 40 to 80 per cent Ni, there is no evidence of any sort of precipitation after conventional treatments, which induce increases of both tensile strength and of hardness amounting to 100 per cent and more. The most striking characteristic, however, of these alloys is that they cannot be overaged. As can be seen from the graphs of Fig. 12,<sup>(33)</sup> maximum hardness is attained by an aging temperature of about 1100° F.; at higher aging temperatures, the hardness decreases substantially. But if these alloys, aged at temperatures above 1100° F. and rapidly cooled, are re-aged at 1100° F., their hardness is restored almost (but not quite) to its maximum value, proving that the diminution occasioned by the prior treatment was due not to overaging or overgrowth of the hardening particles but to their re-solution in the parent lattice. The equilibrium conditions have not been completely worked out, but the known facts suggest the solubility curve shown in Fig. 12.

Although the rates of agglomeration in such alloys—as indicated by the course of age-hardening—are not inconveniently long, 5 to 10 hr. only

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<sup>13</sup> Nickel appears to exercise the same effect in the nickel-tin-copper alloys on the solubility of the beta or delta constituent and perhaps copper exercises this effect in the silicon nickel alloys.

being required for aging at 1100° F., the thermal stability of that assembly of presumably finely dispersed particles of the hardening compound seems to be very great at all temperatures at which the particles are not themselves unstable in their environment. In consequence of this unusual thermal stability, these alloys may be hardened quite satisfactorily by slow cooling from the conventional solution-annealing treatment, and do not absolutely require a second tempering treatment, although such

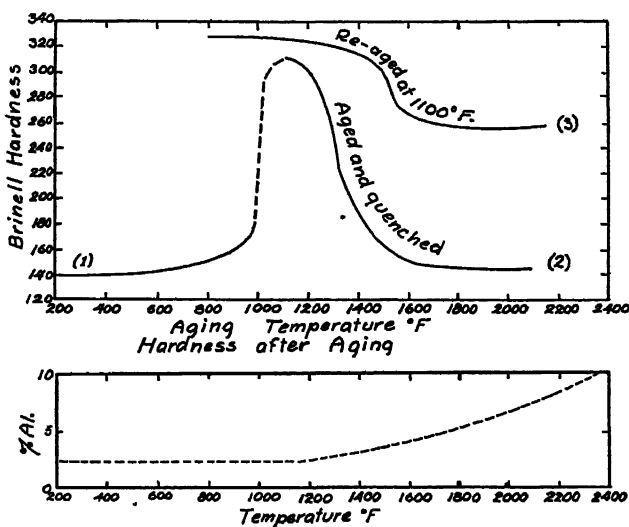


FIG. 12.—AGE-HARDENING OF 4 PER CENT ALUMINUM-COPPER-NICKEL ALLOY AND PROBABLE SOLID SOLUBILITY OF ALUMINUM IN 28 PER CENT COPPER-NICKEL ALLOY (*Mudge*<sup>(33)</sup>).

Curve 1 represents hardness of specimens softened by quenching from 1650° F.; curve 2, aged 1 hr. and quenched and curve 3, re-aged 12 hr. at 1100° F.

treatment ordinarily still further improves their properties. The alloys also retain their hardness and strength remarkably well at elevated temperatures, as will be seen from the curves of Fig. 17.

#### SUPPRESSED TRANSFORMATION HARDENING

An important, although limited, group of alloys may be age-hardened in consequence of their undergoing a phase transformation in the solid state. They respond to the conventional type of dispersion-hardening treatment, which suppresses the transformation at the normal temperature and permits it to proceed at lower ones. This emphasizes the fact that there is of course no real distinction between suppressed-transformation and supersaturated-solution age-hardening. Age-hardening in both has its origin in a suppressed transformation of one character or another.<sup>(34)</sup>

Most, but not all, phase transformations may be made the basis for hardening heat treatments. The most notable of this type of alloy

system, of course, is steel, of which the hardness, after quenching and tempering at moderate intermediate temperatures, is due principally to the presence of  $\text{Fe}_3\text{C}$  particles in fairly high dispersion. Its greater hardness in the martensitic condition, however, probably is due to other causes, which have been much discussed, and will not here be touched upon.

*Aluminum-zinc.*—Some interesting characteristics are displayed by the beta aluminum-zinc alloys, of which the beta phase, assumed by some to correspond to the compound  $\text{Al}_2\text{Zn}_3$ , decomposes at about  $256^\circ\text{C}$ . into a eutectoid of zinc and aluminum-solid-solution. When this transformation is suppressed by rapid cooling, this compound decomposes spontaneously at room temperature<sup>(35,36)</sup> into aluminum and zinc solid solutions, with marked evolution of heat, and at the same time undergoes considerable age-hardening. The transformation somewhat resembles

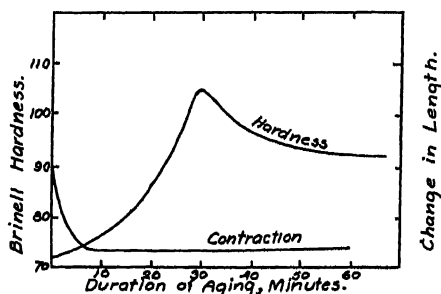


FIG. 13.—CONTRACTION AND HARDNESS DURING ROOM-TEMPERATURE AGING (AFTER QUENCHING) OF 9.5 PER CENT ALUMINUM-ZINC ALLOY (Tanabe<sup>(37)</sup>).

that of steel, since during slow cooling a eutectoid is formed, similar structurally to pearlite; if this eutectoid transformation is suppressed, the constituents of the eutectoid are nevertheless precipitated in fine dispersion, but in quite different geometrical distribution.

The hardening of quenched beta alloys occurs, however, only after the transformation has been partially completed, as is shown in Fig. 13, based upon data by Tanabe;<sup>(37)</sup> the normal contraction in specific volume incident to the separation of the stable phases is practically completed within 10 min., whereas the hardness does not attain its maximum value until after 30 minutes.

Here is perhaps a case in which the optimum particle size for dispersion hardening is substantially greater than that of the first formed particles, which must coalesce before they are able to harden the parent metal, and it offers therefore an interesting contrast to the duralumin system in this respect.

*Copper-gold System.*—A most interesting and instructive system of this type is the gold-copper alloy series which forms at all temperatures above about  $450^\circ\text{C}$ . a continuous series of solid solutions. As shown by

Grube<sup>(38)</sup> and others,<sup>(40)</sup> these solid solutions are transformed at certain temperatures and within certain ranges of composition into compounds,  $\text{CuAu}$  and  $\text{Cu}_3\text{Au}$ , stable at the lower temperatures; the constitutional diagram is shown in Fig. 14.

The  $\text{CuAu}$  compound, when produced by slow cooling or annealing at  $350^\circ\text{C}$ ., is soft and of about the same hardness as that of the quenched solid solution. Yet when the standard age-hardening treatment is

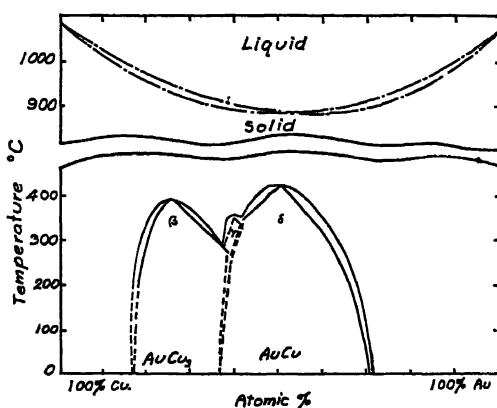


FIG. 14.—CONSTITUTION DIAGRAM OF GOLD-COPPER ALLOYS (Houghton-Payne<sup>(38)</sup> Sterner-Rainer<sup>(40)</sup>).

applied to this composition, very substantial increases of hardness and of strength are induced, which are shown in Fig. 15, taken from data by Nowack.<sup>(41)</sup> These are accompanied by quite normal and continuous changes in the specific volume and in electrical conductivity.

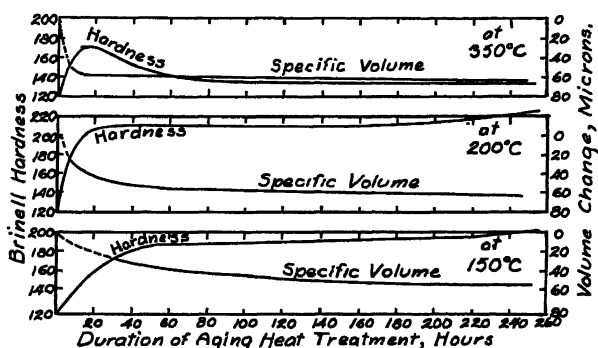


FIG. 15.—HARDNESS AND SPECIFIC VOLUME DURING AGING (AFTER QUENCHING) OF 50 ATOMIC PER CENT GOLD-COPPER ALLOY (Nowack<sup>(41)</sup>).

This transformation involves, it should be observed, not a portion of the metallic lattice, as in the case of simple precipitation hardening, but all of it. It probably does not occur simultaneously nor uniformly throughout each grain of solid solution, but is initiated at local nuclei

centers throughout each grain and proceeds at unequal and varying rates within the different regions of each crystal. In this sense the mechanics of initial age-hardening in this alloy are so similar in nature to that of simple precipitation hardening as to be scarcely distinguishable from it. The strategic location and orientation of fine particles of a compound, no harder than the solid solution itself, appear in this case to produce very substantial hardening and strengthening effects upon the latter.

After the initial stages of age-hardening, and during the completion of the transformation, as reflected in the specific volume, the hardness is probably due to the fine grain size of the precipitating phase and to the orientation of these grains.

Curiously enough, practically no age-hardening occurs in connection with the  $\text{Cu}_3\text{Au}$  transformation, which in many respects is quite similar to that of  $\text{CuAu}$ . The lattice of  $\text{Cu}_3\text{Au}$  is, however, almost identical with that of the solid solution, whereas that of  $\text{CuAu}$  is not<sup>14, (42)</sup>. In consequence, the lattice of the  $\text{Cu}_3\text{Au}$  groups or particles hardly presents any interruption of the parent lattice whereas, with respect to certain planes at least, the parent lattice would be interrupted at the boundary of a  $\text{CuAu}$  particle. These examples, I think, nicely illustrate the great importance of the crystallographic character of age-hardening particles, and of the orientation of their lattices with respect to that of the host lattice.

#### INFLUENCE OF COMPOSITION ON PROPERTIES OF AGE-HARDENING ALLOYS

Attention was earlier called to the universality of age-hardening and to the fact that potentially we are today in position to develop age-hardening alloys upon almost any base composition we please. That we have been able to realize this promise is generously demonstrated by the imposing list of alloys in Table 1. It is evidently not too difficult to develop age-hardening in alloys.

We are not, however, always able to develop in such alloys precisely those properties which we desire, nor even the properties which might be expected of them. For reasons which are still largely obscure, the hardening constituents of many such alloys do not cooperate with the base metal to the best advantage in the development of improved mechanical properties. Let us examine briefly such relations as appear to exist between age-hardening response and the character of the alloy system and its two components—solvent and solute.

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<sup>14</sup> The compound  $\text{CuAu}$  has a face-centered tetragonal lattice (axial ratio 1:07) and the  $\text{Cu}_3\text{Au}$  compound a face-centered cubic lattice similar to the solid solution lattice but of slightly different lattice constant, and in both cases there is an ordered arrangement of copper and of gold atoms, in contrast with the random distribution of such atoms in the solid solution.

In the first place, it is interesting to realize, as the data of Table 2 indicate, that the increases of hardness and of strength, possible in such alloys through age-hardening, are often of the same order of magnitude as those obtained by substantial cold working. This reflects the facts in both cases (1) that these increases are secured through the intervention of obstruction to slip or deformation, and (2) that there is a limit set to the extent of such increases in both cases by the same basic characteristics of the parent lattice. We cannot normally secure the same properties in a soft base metal or alloy as in a harder one, whether by cold working or by dispersion-hardening.

Yet we are not able in some instances even to approach this limit, whereas in others we actually surpass considerably the hardness values of the fully cold-worked base metal. Thus, the hardness of aluminum can be increased from about 60 to 110 Brinell with either  $\text{CuAl}_2$  or  $\text{Mg}_2\text{Si}$  hardener, whereas with either silicon or magnesium it is not possible to increase the Brinell hardness by more than 10 to 15 points Brinell. In the 1 per cent iron-copper age-hardening alloys, the hardness increase during age-hardening amounts to about 20 points only, whereas the 2.5 per cent beryllium-copper alloy may be hardened to about 400 Brinell, a value considerably in excess of that of cold-rolled copper (about 100).

There is thus, even within the limitations imposed by the character of the host lattice itself, a considerable degree of individuality about the age-hardening characteristics of alloy systems, the precise reasons for which we have difficulty in understanding. The optimum development of age-hardening is to be expected, of course; (1) when the hardening constituent is itself hard or, more accurately, effective in resisting or preventing slip, (2) when the volume of the segregated constituent is large and (3) when the growth and coalescence of the segregated particles may be arrested in their early stages, yielding a fine rather than a coarse dispersion.<sup>15</sup>

*The Hardening Constituent.*—The hardening constituent in most of the good age-hardening alloys is itself considerably harder than the

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<sup>15</sup> It is hardly necessary to mention that it is a fundamental condition for age-hardening that diffusion and segregation must actually occur at temperatures below those of the fundamental transformation. It is not impossible that there exist alloys which have "suppressed age-hardening characteristics" in consequence of the fact that the necessary aging temperatures are below those at which diffusion can occur.

Fortunately, diffusion appears to take place at relatively low temperatures in most alloys, and indeed even at temperatures much below those at which that kind of atomic mobility is manifest, which is responsible for recrystallization and grain growth. The diffusion of copper atoms at ordinary temperatures in the lattice of pure aluminum is a good example of this fact, since aluminum does not normally recrystallize below about 200° C. An even more striking case is that of the age-hardening at room temperatures of low carbon-iron alloy, demonstrated by Köster,<sup>(12)</sup> and which we may consider to be due to the formation of cementite particles or "knots" by diffusion of carbon atoms.



base metal, and one can hardly escape the conclusion that hard constituents are generally desirable for this purpose. However, they are not necessary, and in some cases substantial age-hardening is achieved with comparatively soft constituents. The 7.5 per cent copper-silver alloy, for example, is substantially hardened by the precipitation of copper solid solution, which is itself quite soft; the hardness and strength of such an alloy may be increased from 60 to 120 Brinell and from about 17 to 24 tons per sq. in. respectively.<sup>(44)</sup> The comparatively soft compound, AuCu, in the 50 atomic per cent gold-copper system, renders the alloy quite hard and strong when present in dispersed or other form resulting from precipitation and aging at intermediate temperatures.

The behavior of these alloys emphasizes a most important aspect of age-hardening, which was pointed out by Archer<sup>(45)</sup> and by Mehl.<sup>(46)</sup> The potency of a hardening constituent need not depend wholly upon its average mechanical properties but is primarily determined by the effectiveness of its dispersed particles in resisting or preventing slip in their host lattice. This in turn may be greatly dependent upon their shape and upon their crystallographic orientation with respect to this lattice, as well as upon their intrinsic hardness. Investigations such as those by Mehl and his associates into the crystallographic character of precipitation within solid solutions must yield us greater insight into the true nature of age-hardening.

The amount of the precipitated constituent, as determined primarily by the solubility relations, is likewise important; other things being equal, large volumes of dispersed precipitate will harden more effectively than small ones. In the 50 atomic per cent gold-copper system, the softness and relative ineffectiveness of the hardening phase is partly balanced by its large amount. No doubt this sort of compensation is generally possible. Partly because of their greater volume per atom of the hardening element, hardening constituents containing a large proportion of atoms of the host lattice are usually more effective than those consisting wholly of stranger atoms; 2 per cent of copper precipitating<sup>16</sup> as  $(\text{CuAl}_2)$  is more effective in hardening aluminum, for example, than 2 per cent of precipitated silicon.

It is likely that there are other reasons why such constituents often are more effective "hardeners" than others, particularly in the cases of homogeneous or "knot" hardening alloys; reasons intimately related to the mechanism of formation, segregation and orientation of such particles in the host lattice.

*Arrest of Particle Growth.*—When the influence of particle hardness and of volume of precipitate is fully discounted, there still remain unexplained many striking cases of deficient as well as of excessive age-hardening in

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<sup>16</sup> No distinction is made between actual precipitation and segregation preparatory thereto for the purpose of these and other arguments immediately preceding.

systems in which normal age-hardening would be expected. Thus a saturated magnesium-aluminum alloy may precipitate more than 20 per cent by volume of the (presumably) hard beta compound; yet in consequence it may be age-hardened only by about 15 points Brinell. This may be compared with the volume of precipitated  $\text{CuAl}_2$ , about 5.5 per cent, which induces substantial hardening in copper-aluminum alloy.<sup>17</sup> On the other hand hardening in the beryllium-copper and the beryllium-nickel alloys much exceeds the usual limits of age-hardening.

The explanation for the abnormal behavior of such alloys probably is to be found in the conditions which govern the growth and coalescence of particles—whether crystalline or otherwise. Alloys in which this growth is readily arrested at small particle sizes exhibit optimum capacity to age-harden; those in which the temperature ranges of rapid particle growth substantially overlap those in which diffusion and particle formation may occur fail to develop marked age-hardening,<sup>18</sup> in consequence of the neutralizing effect of overaging.

The reluctance of good age-hardening alloys to "overage" is thus a most important and a rather arresting fact. What may be the reason for their inertia in this respect?

Although diffusion may take place readily, even at room temperatures, in pure 5 per cent copper-aluminum alloy, marked coalescence of  $\text{CuAl}_2$  particles causing overaging takes place only at temperatures about 200° C. higher, and similar relations hold in the case of most age-hardening alloys. The low velocity of overaging cannot generally be due therefore to the low velocity of atomic diffusion.

It may be due partly to interference with the process of nucleus formation and precipitation, and to the fact that a minimum number of molecules must assemble before such a nucleus can be formed and can precipitate; although the precise nature of this interference is still very obscure. In 5 per cent copper-aluminum alloy overaging apparently cannot occur below about 200° C. and this is the minimum temperature at which crystalline particles of  $\text{CuAl}_2$  may form. Apparently "knots" cannot overage. In the magnesium-silicon-aluminum alloy, the  $\text{Mg}_2\text{Si}$  particles precipitate at room temperatures but possibly do not form at these temperatures a crystalline lattice, susceptible to further growth, and in this case also, overaging does not occur below about 150° to 200° C.<sup>19</sup>

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<sup>17</sup> One would expect also greater hardness increase during the aging of 50 atomic per cent silver-aluminum alloy than that actually shown by test.<sup>(47)</sup>

<sup>18</sup> It should be interesting to ascertain whether failure of age-hardening to develop in some cases, even under apparently favorable conditions, might be reflected in unusually narrow aging temperature ranges.

<sup>19</sup> One may well ask at this point whether "knot-like" particles can cause as great increases in hardness as discrete, precipitated crystalline particles. In so far as evi-

I believe, however, that the arrest of particle growth at any particular stage, whether of "knots" or of crystalline particles, is principally caused by a sort of dynamic diffusion equilibrium reached by the host of uniformly fine and uniformly distributed particles; an equilibrium similar to that in the grain size of annealed cold-worked metals. In this sense it is the uniformity of particle size, shape and orientation and of their distribution which, at any temperature, acts as a barrier to their further growth. And the motive power, if you please, for such growth is furnished by the differences only, with respect to these characteristics, which exist between the various particles.<sup>20</sup> Those alloys in which there is a considerable degree of uniformity, with respect to particle size and distribution, among the hardening particles in the early stages of their development will not readily overage; those in which considerable disparity exists in this respect will overage.

What the precise conditions are that lead to variations in the uniformity of these factors are not known. Probably the uniformity of atomic dispersion in the original supersaturated solid solution is pertinent in this respect. It may be found that stranger atoms which are unlike those of the base lattice, particularly in size, may be disposed to arrange themselves more uniformly in the original saturated solution than atoms which are similar to those of the base metal, and hence might develop a more growth-resistant host of disperse particles during subsequent aging. It should be noted, also, that resistance to overaging is very striking in such alloys as aluminum-copper-nickel and in the "Konal" alloy series, suggesting that ternary or multiple atom constituents, requiring diffusion of a more complex nature for their growth, may be expected to be more stable in fine dispersion than binary or elemental ones.

If resistance to overaging is thus determined by the sort of dynamic equilibrium just pictured, it should be possible to influence it substantially by the introduction of other elements into the solid solution, which would alter the uniformity of distribution of lattice disturbances throughout the supersaturated solution.

*Tensile Strength and Hardness.*—The hardness and the tensile strength of age-hardening alloys have so far been considered together, since normally we expect, and indeed usually find, general correspondence

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dence is available on this point, it appears that crystalline particles generally induce greater hardness increases than do particles in earlier stages of formation. In many specimens of duralumin and of copper-aluminum alloys, however, which have been investigated, the hardness, previous to CuAl<sub>2</sub> precipitation, rises to values at least equal to and in many cases superior to those reached after such precipitation. "Knots" therefore in some cases may be almost equally efficacious in hardening as precipitated crystalline particles.

<sup>20</sup> It should be observed that the characteristics which are determining in this respect include also the extent and character of the local lattice distortion around each particle.

between the two. In some cases, however, there is little or no increase in tensile strength during age-hardening. This is true of the 1 per cent iron-copper alloy,<sup>(46)</sup> and a more striking illustration is found in the 50 per cent aluminum-silver alloy, as shown by Archer and Kempf.<sup>(47)</sup> An increase of hardness from 89 to 110, during the aging of this alloy, was accompanied by an actual decrease of tensile strength from 51,000 to 48,000 lb. per sq. in. Even in those alloys exhibiting parallel increases in strength and hardness, the optimum values for the two are not always developed at the same aging temperature—as illustrated by the case of standard sterling silver (Norbury<sup>(44)</sup>).

In the iron-copper alloy the hardening constituent, iron, is not much harder than the matrix itself, and its power to obstruct and divert slip is perhaps exhausted after those earlier stages of deformation, during which Brinell hardness is measured. The tensile strength is a reflection of the behavior of metals during later stages of deformation, when certain types of interfering particles may no longer be effective. Perhaps we should expect parallelism of Brinell hardness values and of tensile stress only at some intermediate value of the applied strain.

It is also possible that Smekal's suggestion discussed by Professor Bridgman<sup>(48)</sup> may have an important bearing on this matter, that metals and alloys contain a multitude of small voids; these would certainly affect tensile strength to a greater extent than hardness. The precipitation of hardening particles in fine dispersion could easily give rise to the existence of such voids, the extent and distribution of which undoubtedly would vary substantially in different alloy systems. The observed changes of specific volume and of lattice constant during the high-temperature aging (200° C.) of 5 per cent copper-aluminum alloy, indeed, point strongly to the existence of such voids, since the total expansion during aging is greater than that calculated from the lattice expansion and the contraction of the regions forming  $\text{CuAl}_2$ . The tensile strength during such high-temperature aging also is not maintained at a level comparable with the hardness.

*Plasticity.*—The normal increases of hardness and of strength occurring during the age-hardening of alloys are usually accompanied by a corresponding decrease in ductility, which is variable in amount. It is extreme, for example, in the 2.5 per cent beryllium-copper alloy,<sup>(49)</sup> of which the elongation decreases from about 50 to 1 per cent during aging, while the hardness increases from about 100 to 400 Brinell. In many cases, such as the aluminum-copper-nickel and the nickel-silicon-copper alloys, the decrease in ductility is only moderate. In duralumin, the elongation remains practically unchanged during room-temperature aging, although its plasticity—its susceptibility to cold forming operations—is substantially diminished thereby.

This variation in behavior undoubtedly is partly due to the variation in the extent to which precipitation takes place at grain boundaries, but we shall probably not find its full explanation until we understand better the nature and the crystallographic orientation of hardening particles in such systems. It is significant, however, that this diminution of ductility appears to be less, the less advanced is the state of precipitation and coalescence of the hardening particles required for full hardening. Those systems in which full hardening occurs when the particles are still in a transition state, and not fully precipitated in crystalline form, exhibit, on the whole, better ductility in the full-hard condition than systems in which we believe the hardening particles to have precipitated and crystallized. Duralumin, aged and hardened at temperatures in the neighborhood of 125° to 175° C., also suffers considerably in ductility, as shown by the data of Meissner<sup>(9)</sup> in Table 3. As the precipitating particles actually begin to form the new lattice, both within and at the grain boundaries, their adverse effect upon ductility becomes increasingly dominant.<sup>21</sup> Possibly the "knot" type of particle resists slip on the glide planes but does not like a crystalline particle entirely prevent it, and consequently exhaust earlier the capacity of the metal to deform.

I should like incidentally to point out that this decrease in ductility of duralumin aged at 125° to 175° C., occurring at temperatures below those at which the lattice parameter and the specific volume increase, nevertheless strongly suggests that the process of precipitation

TABLE 3.—*Properties of Duralumin Aged 20 Hr. at Various Temperatures after Quenching and Aging at Room Temperatures*  
(Cu 4.2%; Mg 0.5%; Si 0.3%) (Meissner <sup>(49)</sup>)

	50° C.	125° C.	160° C.	200° C.
Brinell hardness.....	120	118	126	121
Tensile strength, tons per sq. in.....	38.6	38.0	44.0	38.0
Yield point.....	23.3	22.2	38.0	32.0
Elongation.....	20.0	21.0	7.0	7.0

is under way; perhaps at these temperatures some disregistry of atom planes, between the "knot" regions and the surrounding lattice, has already occurred.

*Fatigue Strength.*—There is one "mechanical property" of age-hardening alloys which does not appear to profit proportionately from heat treatment. As Moore<sup>(50)</sup> and McAdam<sup>(51)</sup> have shown, the fatigue limit of

<sup>21</sup> Yet the hardening of Mg-Si-Al alloy is probably due to actual precipitation of some constituent (possibly Mg<sub>2</sub>Si) and its ductility is not altered during room-temperature aging; the hardening particle is probably not crystalline; however.

annealed duralumin may increase from 10 to 50 per cent during normal treatments which induce increases in hardness and strength of 100 per cent. It appears that this is true also of 4 per cent aluminum-copper-nickel alloy and of the nickel-silicon-copper alloys, according to the results of unpublished researches by McAdam. This reminds us of the effect of cold working on fatigue strength, which is also much less effective in increasing fatigue strength than in increasing the yield point and tensile strength of metals and alloys generally.

Although Smekal's hypothesis of internal voids should not be lost sight of in this connection, one can hardly escape the conviction that internal stresses are here at work. The latter certainly play a part in preventing the full development of fatigue strength in cold-worked metals, as has been indicated by McAdam.<sup>(52)</sup>

These internal stresses in age-hardened metals are highly localized and probably roughly symmetrical in direction and intensity to the hardening "knots" or particles themselves. Consider for a moment the possibilities for their development during a transformation in which the particle region contracts and its surrounding matrix expands, as in copper-aluminum, or the converse, which appears to be true in the beryllium-copper alloy.<sup>22</sup>

The presence of such stresses is suggested by the character of that portion of the stress-strain curve below the yield point, observed in some age-hardened alloys. Not only do they affect the fatigue strength but they are probably of considerable importance in connection with the alteration in other properties which occur during aging.

#### STRENGTH AT ELEVATED TEMPERATURES

One of the valuable features of some age-hardening alloys is the stability of their strength and hardness at higher temperatures. Provided the temperature in question is not equal to or greater than that at which overaging proceeds, these alloys are likely to retain their hardness and strength at temperatures well above room temperature. In fact, within their age-hardening temperature ranges they tend to become, not weaker and softer as time progresses, but actually harder. This is nicely illustrated in the 4 per cent aluminum-copper-nickel alloy, which exhibited no creep during a several hour test at 800° F. when subjected to a load of 100,000 lb. per sq. in., although the elastic limit of the base copper-nickel alloy at this temperature is approximately 25,000 lb. per sq. in. only.<sup>(53)</sup> Such alloys obviously are well suited for certain types of high-temperature

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<sup>22</sup> Note that Mg<sub>2</sub>Si apparently precipitates during room-temperature aging with expansion of the lattice region comprising the magnesium and silicon atoms, but with little change in the aluminum lattice, whereas CuAl<sub>2</sub> cannot precipitate at room temperature, the precipitation being accompanied by contraction of that region, in spite of the fact that the aluminum lattice itself expands when CuAl<sub>2</sub> does precipitate.

service and one such alloy today is actually utilized in this manner; the titanium-cobalt-nickel-iron alloy called "Konel" alloy, developed by the Research Department of Westinghouse Electric & Manufacturing Co. The aging temperature range of these alloys lies between 600° and 700° C. and some of them exhibit proportional limits of about 60,000 lb. per sq. in. at a temperature of 600°C.—remarkable values for any metallic material.<sup>(53)</sup>

#### EFFECT OF DISPERSION-HARDENING ADDITIONS UPON OTHER PHYSICAL PROPERTIES

One of the important and favorable aspects of the "dispersion" method of hardening alloys is the fact that the metallic additions required in any given case may usually be relatively small in amount. If skilfully chosen they may exert, therefore, only a modest effect upon the other properties of the base alloy in question—although profoundly altering its mechanical properties. This *selective* feature of "dispersion-hardening" appeals to me as of considerable practical value.

As indicated in Table 1, the amounts of hardening additions required for age-hardening vary from as little as 0.04 per cent in the calcium-lead alloys to as much as 25 per cent in the molybdenum-iron. In many prominent alloys these amounts do not exceed 5 to 6 per cent and may be as little as 2.5 per cent; even such amounts do not generally adversely affect the other characteristics of the base alloy. In order to use as small an amount of hardening elements as possible, it is desirable to use such elements as combine with the base alloy atoms to form the hardening constituent.

Thus such fundamental and periodic properties as thermal expansion and the elastic moduli of age-hardening alloys are generally quite similar to those of the metals upon which they are based, the beryllium-copper alloy constituting an apparent exception in this respect, exhibiting a substantial increase in the elastic modulus during age-hardening and amounting to about 40 per cent.

Even the sensitive electrical properties of high-conductivity metals may be better maintained when hardened by this method than when hardened by elements entering into solid solution, as was emphasized by Corson<sup>(54)</sup> in connection with his investigations of the chromium-silicon and nickel-silicon-copper alloys. With properly chosen and balanced hardening agents, the metallic matrix may be left substantially free from dissolved stranger atoms after full hardening.

The corrosion resistance of age-hardening alloys is also substantially similar to that of their base alloys, provided the hardening additions do not exceed about 5 per cent in amount.

#### INTERGRANULAR PRECIPITATION

There is one structural defect from which all age-hardening alloys suffer to a greater or less extent. Precipitation of the hardening consti-

uent under optimum aging conditions is probably always accompanied by some intergranular precipitation. In some cases this is prominent enough to impair in some respects the properties of the hardened alloy.

In duralumin this leads to intercrystalline corrosion and embrittlement in some environments, and protection against this defect has been secured in the well-known aluminum-clad duralumin products. Intergranular precipitation in duralumin is more pronounced during aging at high temperatures (120° to 200° C.) than at lower or ordinary ones, and in consequence the susceptibility to intercrystalline corrosion and embrittlement may be lessened by employing low aging temperatures, probably a rule of general applicability.

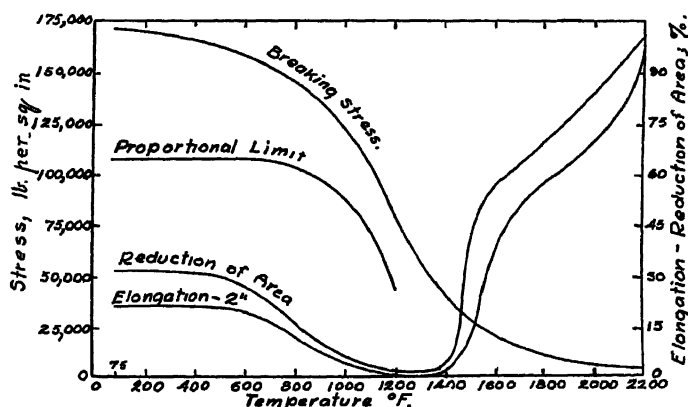


FIG. 16.—MECHANICAL PROPERTIES OF ALUMINUM-COPPER-NICKEL ALLOY AT HIGH TEMPERATURES (*Mudge*<sup>(21)</sup>).

Short-time tests of 5 per cent aluminum-copper-nickel alloy (copper about 28 per cent) tested in "aged" and full-hard condition.

Aborn and Bain<sup>(25)</sup> have pointed out another interesting demonstration of this phenomenon in the corrosion-embrittlement of the 18-8 austenitic chromium-nickel-iron alloy, due apparently to the intergranular precipitation of chromium carbide, and the impoverishment of adjacent regions in chromium content, permitting rapid corrosion and penetration.

Intergranular precipitation sometimes affects adversely the plasticity of alloys within the temperature range of aging, and in consequence impairs their hot-working properties. This is illustrated in Fig. 16, showing the ductility at higher temperatures and particularly within the aging temperature range of 4 per cent aluminum-copper-nickel alloy.

Indeed, it is not improbable that many other cases of intercrystalline brittleness within intermediate temperature ranges may be due to the intergranular precipitation of some constituent or impurity of the alloy—even when this precipitation is too slight to confer definite, age-hardening properties. The temper brittleness of steels is probably an example of



this phenomenon. This is one of the disadvantages which we have to accept along with the advantages of alloys showing variations of solid solubility with temperature.

### HEAT TREATMENT OF AGE-HARDENING ALLOYS

The optimum mechanical properties of age-hardening alloys are normally developed in them by a combination of the conventional homogenizing or "solution" annealing treatment and quench, followed by the hardening aging treatment at lower temperatures.

As might be expected, the range of these aging temperatures is often similar to that of recrystallization of the alloy. It is, however, sometimes lower than this range, as in duralumin and carbon-iron. In some cases it is greater. Thus in the 1 per cent iron-copper alloys studied by Hanson and Ford<sup>(40)</sup> full age-hardening requires a temperature of 500° C.,<sup>23</sup> whereas the recrystallization temperature range of these alloys probably is much lower, since that of pure copper lies between 200° and 350° C. Whether it is diffusion or the rate of nucleus formation, which in this case is sluggish below 500° C., is not yet known.

The aging process can however be affected by the temperature of prior solution annealing as well as by the rate of cooling from that temperature. Normally, it is necessary to homogenize any such alloy only just above the temperature at which the hardening elements are entirely dissolved in solid solution. In the zinc-aluminum alloys,<sup>(6)</sup> however, it is necessary to anneal and quench from temperatures substantially higher than this in order to develop age-hardening at all. That this is not due to sluggish dissolution and diffusion at high temperatures is indicated by the fact that age-hardening, and presumably therefore diffusion, takes place fairly readily at the lower temperatures of aging. Presumably the higher quenching temperature in this case serves better to suppress the transformation during the first quenching treatment and consequently permits better the later development of the aging process.

Similarly, as has been pointed out by Dean<sup>(61)</sup> and others,<sup>(62)</sup> the hardness values secured during aging at any temperature may be altered substantially by varying the rate of quenching prior to aging. Undoubtedly some atomic segregation of the hardening constituent takes place during quenching, which affects not only the subsequent course of diffusion but the equilibrium distribution of segregation, as well, attained after such diffusion.

*Acceleration and Retardation of Age-hardening.*—One of the most interesting and significant features of age-hardening is the demonstrated possibility in some cases of accelerating or retarding the course of age-

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<sup>23</sup> The change in solubility of iron in copper occurs between 750° and 1050° C.; the iron-copper solid solution is therefore supersaturated and potentially age-hardenable at all temperatures lower than 750° C.

hardening. Schmid and Wassermann<sup>(9)</sup> have shown that the aging of duralumin at room temperature may be substantially hastened by cold working immediately after quenching, an operation which may be

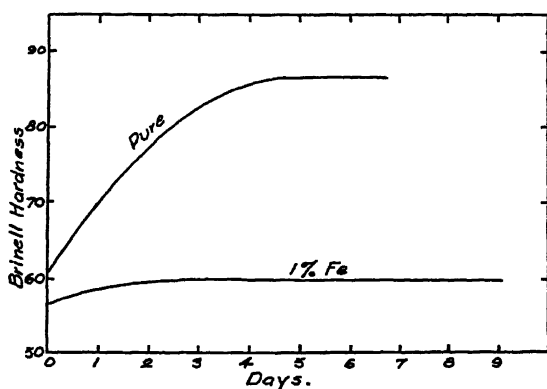


FIG. 17.—“RESTRICTION” OF ROOM-TEMPERATURE AGING OF PURE 5 PER CENT COPPER-ALUMINUM ALLOY BY ADDITION OF IRON (Fraenkel<sup>(6)</sup>).

expected to increase the mobility and the average rate of diffusion of the copper atoms.

But more interesting and unexpected is the fact that the addition of other elements may also affect the aging properties of duralumin and other age-hardening alloys. As shown in Figs. 17 and 18, the addition

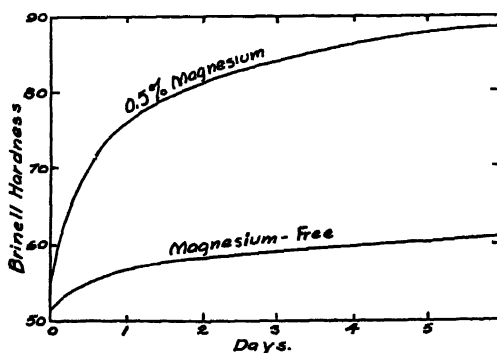


FIG. 18.—“EXTENSION” OF ROOM-TEMPERATURE AGING OF IRON-BEARING 4 PER CENT COPPER-ALUMINUM ALLOY BY ADDITION OF MAGNESIUM (Fraenkel<sup>(6)</sup>).

of iron retards the room-temperature aging of pure copper-aluminum alloy, whereas that of magnesium or of lithium accelerates it,<sup>(6,56,65)</sup> and restores the capacity of iron-bearing copper-aluminum to age-harden at room temperatures.<sup>24</sup>

<sup>24</sup> It is not quite clear from the published data which of these effects of magnesium is the more prominent. It may be that magnesium and lithium react primarily with the iron content of slightly impure copper-aluminum alloy and thus undo its retarding influence on the room-temperature aging of pure copper-aluminum.

Masing<sup>(26)</sup> has shown that 0.1 per cent phosphorous lowers the aging temperature range of the beryllium-copper alloys and Seljesater<sup>(27)</sup> describes the retarding effect of arsenic additions upon the aging of antimony-lead alloys. The effect of small additions of magnesium and of tin in retarding and accelerating respectively the transformation of the aluminum-zinc alloys<sup>(28)</sup> containing the beta phase is another illustration of this interesting phenomenon.

The effect of these additions appears to be that of increasing or decreasing the extent of hardening throughout the lower aging-temperature ranges; they do not seem to alter markedly the velocity of such hardening as can occur at any particular temperature. Properly speaking, therefore, they should not be regarded as accelerators and retarders of age-hardening but rather as "extenders" or "suppressers" of it.

Various explanations have been offered for these phenomena, although their precise mechanism still remains obscure. Archer<sup>(29)</sup> considers the effect of magnesium on the room-temperature hardening of duralumin to be due to its effect in distending the aluminum lattice and thus permitting more readily the diffusion of copper atoms. Seljesater<sup>(27)</sup> emphasizes the possibility of the adsorption of arsenic atoms on the surfaces of the precipitated antimony particles, forming a surface layer which impedes further growth.

It is probable that both types of effects may be operative, and that the addition of a third element to an age-hardening alloy may either affect the lattice in such a manner as to influence diffusion or may combine with the hardening constituent in such a manner as to affect nucleus formation and growth or as to affect its solubility relations. I believe, however, that the effect of such additions, particularly those which favor hardening, may largely lie in their relation to the dynamic diffusion equilibrium of the "knots" or nuclei in the very early stages of their genesis. Stranger atoms, particularly those quite unlike the parent lattice atoms, may alter considerably the distribution of those irregularities in the supersaturated solution lattice, which serve as starting points for segregation, or might themselves serve as starting points and may thus facilitate segregation; conversely they might so distort the lattice as to render nucleus formation difficult.<sup>25</sup>

Whatever may be the complete explanation of the effect of these "catalyzing" agents for age-hardening, the fact that we may so alter age-hardening processes is probably destined to be of considerable prac-

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<sup>25</sup> It seems at first difficult to account for the pronounced retarding effect on the aging of duralumin of iron, of which the solubility in aluminum is probably less than 0.01 per cent. It is thus present in a rather unfavorable atomic distribution for the purpose of exerting any considerable effect either upon the host lattice or upon the hardening particles themselves. It is not improbable, however, that the solubility of iron in supersaturated duralumin may be greater than that in pure aluminum.

tical importance in the development of useful hardenable alloys and it broadens substantially the means at our disposal for so doing.

### CONCLUSION

I have attempted to show that the past decade has brought us a greatly broadened realization of the effect of internal structure upon the properties of metals and alloys, and that we recognize today more structural types of alloys than we had before imagined. The continued progress which we shall make in our understanding of their structural relations must bring with it substantial advances in our practical utilization of metals, many of which we are not now able wholly to envisage. On the other hand, the study of the effect of heat treatment upon the physical characteristics of age-hardening alloys is bound also to afford us much needed enlightenment as to the intimate structure of, and the local movements occurring within, metallic aggregates. It is for the purpose of emphasizing also this useful aspect of age-hardening and possibly to stimulate further fundamental research with respect to it, that I have ventured to indulge, perhaps to overindulge, in speculation concerning the nature of the age-hardening process.

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## Age-hardening Copper-titanium Alloys

By F. R. HENSEL\* AND E. I. LARSEN,\* EAST PITTSBURGH, PA.

(Boston Meeting, September, 1931)

ACCORDING to statements by Guertler,<sup>1</sup> Smith and Hamilton were the first to study the copper-titanium alloys, but owing to the presence of large amounts of impurities their data are inconclusive. M. A. Hunter and I. W. Bacon later investigated the electrical conductivity and the temperature coefficients at room temperature. The present writers reported their results<sup>2</sup> in November, 1930. Recently Kroll published data on copper-titanium alloys<sup>3</sup> which agree closely with those obtained by the authors.

### MATERIAL TESTED

The titanium used was in the form of square sintered rods, the analysis of which runs as follows: titanium, 95.4 per cent; silicon, 0.7; iron, 1.8; aluminum, 1.4; copper, 0.1; manganese, 0.05. The ingots were prepared in a high-frequency induction furnace in air atmosphere. Their analyses are given in Table 1. Up to 5 per cent titanium the alloys could be forged. Above that amount they were red short and broke up easily.

Owing to their rapid absorption of nitrogen and oxygen from the air, the alloys with the higher amounts of titanium tend to form surface films which greatly increase the casting difficulties, especially when small masses of metal are handled. It was, however, possible to prepare sound ingots up to 25 per cent titanium.

### THERMAL AND X-RAY INVESTIGATION

The cooling curves of some of the alloys are plotted in Fig. 1, and a tentative diagram constructed from these data is given in Fig. 2. From this it is evident that the solid solubility of copper for titanium is approximately 4 to 5 weight per cent titanium at 878° C., which is the eutectic temperature. The melting point of copper is lowered gradually by adding

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<sup>1</sup> W. M. Guertler: *Metallographie*, Erster Band, 390. Berlin, 1912. Gebrüder Borntraeger.

<sup>2</sup> F. R. Hensel and E. I. Larsen, in Westinghouse Elec. & Mfg. Co. *Research Rept.* R-7417-F (Unpublished).

<sup>3</sup> W. Kroll: Vergütbare Titan-Kupferlegierungen. *Ztsch. f. Metallkunde* (1913) 23, 33.



TABLE 1.—*Analyses of Ingots*

Ingot Mark	Cu, Per Cent	Ti, Per Cent	Fe, Per Cent	Al, Per Cent	Si, Per Cent	Mn, Per Cent
0	99.08	0.83	0.05	0.03	0.006	0.007
1	97.15	2.74	0.04	0.06	0.01	0.007
2	95.01	4.74	0.10	0.12	0.02	0.01
3	91.93	7.72	0.14	0.17	0.03	0.012
4	90.54	8.83	0.36	0.20	0.05	0.02
5	84.56	14.28	0.88	0.15	0.09	0.04
6	76.95	20.53	2.01	0.21	0.24	0.06
7	68.96	27.27	3.25	0.24	0.22	0.06
X		2.58				
96	98.40	1.50	0.04	0.03	0.005	0.02
95	97.06	2.90	0.06	0.09	0.007	0.04
16	84.05	15.42	0.50	0.06	0.04	
17	83.08	16.22	0.50	0.07	0.04	
18	82.00	17.31	0.50	0.08	0.04	

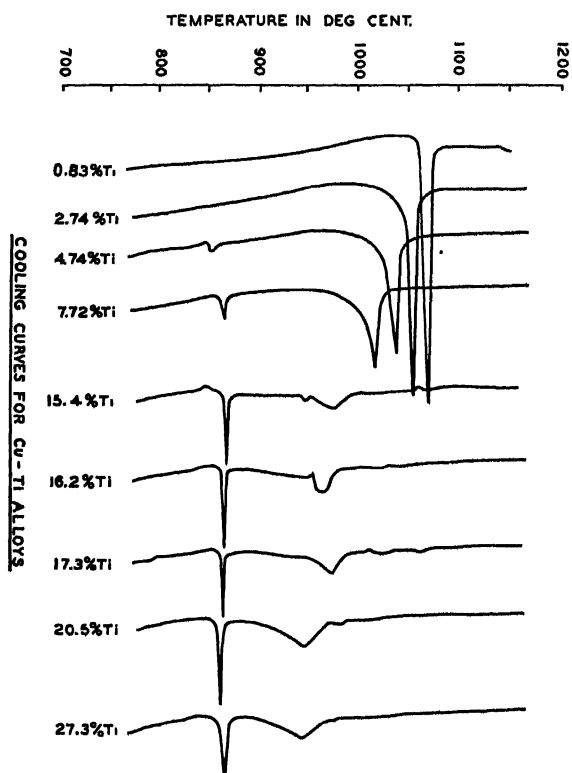


FIG. 1.—COOLING CURVES OF ALLOYS.

more and more titanium. It is probable that the eutectic concentration lies between 20 and 27 per cent titanium.

The results of the X-ray investigation of the as-cast samples are given in Table 2. X-ray pictures of pure copper and pure titanium were made for comparison. The table gives the various spacings of the lattice planes in Ångströms. The last column gives the indices of the planes, obtained by means of the Davey charts (*General Electric Review*, September, 1922). The lines marked SS belong to a cubic face-centered space lattice.

The lines belonging to a face-centered cube are the strongest on all pictures. The lattice constant of this cubic lattice increases slightly with increasing percentage of titanium and ranges from 3.60 Å for pure

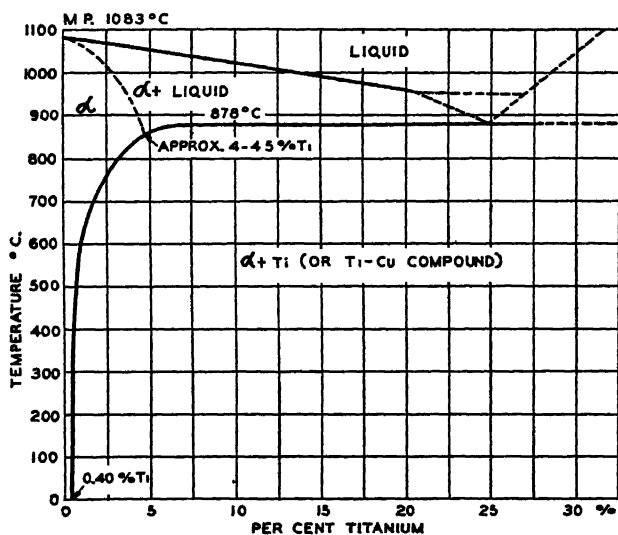


FIG. 2.—TENTATIVE DIAGRAM CONSTRUCTED FROM CURVES OF FIG. 1.

copper to 3.65 for alloy 6. This indicates that a copper-titanium solid solution is formed which has the same space lattice as pure copper. With increasing amounts of titanium some new lines gradually appear, most of which correspond to pure titanium. The first new lines appear in alloy 3, which has a titanium content of 7.72 per cent. The conclusion, however, that pure titanium is precipitated must be made with caution because some of the lines, although fitting very well in the titanium lattice, either do not show at all on the picture of pure titanium, or appear there as very faint lines. This leaves the possibility open that some of those extra lines may belong to a copper-titanium compound. The lines in alloy 7 were very broad and diffuse, a condition which might have been caused by a segregation of titanium within the crystals of the solid solution of titanium in copper.



## AGING TESTS

From experiences with other titanium alloys it was expected that copper-titanium alloys also would age within certain concentration limits. This was verified by a series of experiments in which some of the alloys were quenched from 900° C. and aged at various temperatures for one hour at each temperature. The curve obtained for alloy X with 2.58 per cent titanium is shown in Fig. 3. This indicates that aging starts at 250° C., that the optimum aging temperature is 400° to 450° C., and that above 500° C., the hardness decreases.

The time-hardness curves are given for alloys 0, X and 2 in Figs. 4, 5 and 6. The aging temperatures chosen were 400° and 450° C. With the alloy containing 0.83 per cent Ti the hardness increases rapidly within the first 15 hr. and remains nearly constant thereafter.

No decrease of hardness can be noticed within the first 100 hr.

The hardness at 400° C. aging temperature (125 V.P.N.) is higher than at 450° C., where the maximum hardness reached is 110 V.P.N. In the

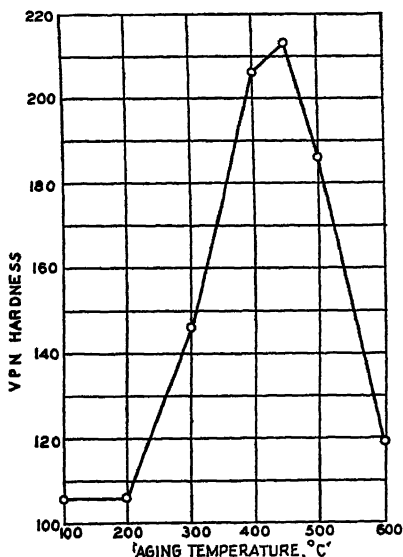


FIG. 3.—CURVE FOR ALLOY X, CONTAINING 2.58 PER CENT TITANIUM.

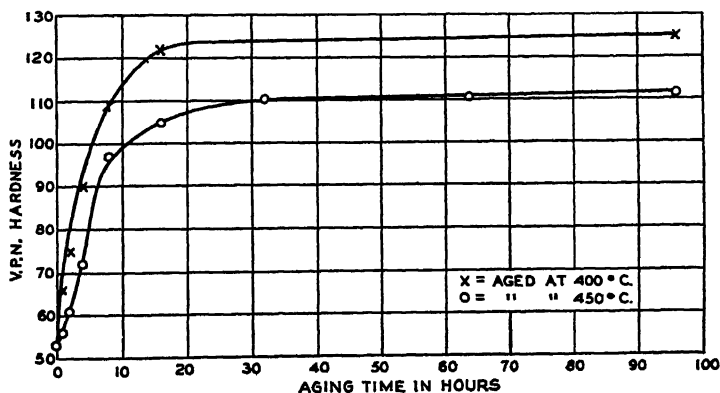


FIG. 4.—TIME-HARDNESS CURVE FOR ALLOY 0, CONTAINING 0.83 PER CENT TI.

alloy with 2.58 per cent Ti (Fig. 5) the hardness curves for 400° C. aging temperature reach a higher but (regarding time) a later maximum than

the curve for 450° C. In both cases the hardness falls considerably after 30 hr. aging time and thereafter remains fairly constant.

The curves for the alloy containing 4.74 per cent Ti reach about the same maximum hardness as for those with 2.58 per cent Ti, the only difference being that the curve for 450° C. reaches its maximum after 7 hr. and the curve for 400° C. aging temperature after 16 hr. There is a rapid decrease in hardness after the maximum to nearly the same value as that found after the original quench. The progress of aging at lower temperatures can be seen in Table 3.

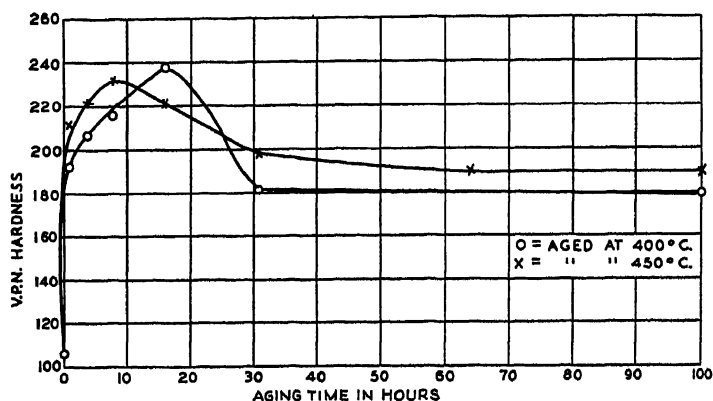


FIG. 5.—TIME-HARDNESS CURVE FOR ALLOY X, CONTAINING 2.58 PER CENT TI.

TABLE 3.—Aging of Sample X, Containing 2.58 Per Cent Titanium

Aging Time, Hr.	V.P.N. Hardness	
	At 300° C.	At 350° C.
As quenched from 950° C.	106	106
1	115	133
2	144	169
3	156	176
4	158	178
5	165	188
6	154	194
8	158	207
10	169	208
30	177	211
100	189	225

### PHYSICAL PROPERTIES

*Electrical Conductivity.*—The electrical conductivity was determined on forged samples. Data on alloys 0, 1 and 2 after quenching from 900° C. and aging to maximum hardness (16 hr.) at 400° C. are given

in Table 4. The quenching produces a supersaturated solution and gives the highest resistivity values, while as a result of aging a precipitation of the substances held in solid solution occurs whereby the resistivity is greatly reduced. The results are plotted in Fig. 7. It can be seen that

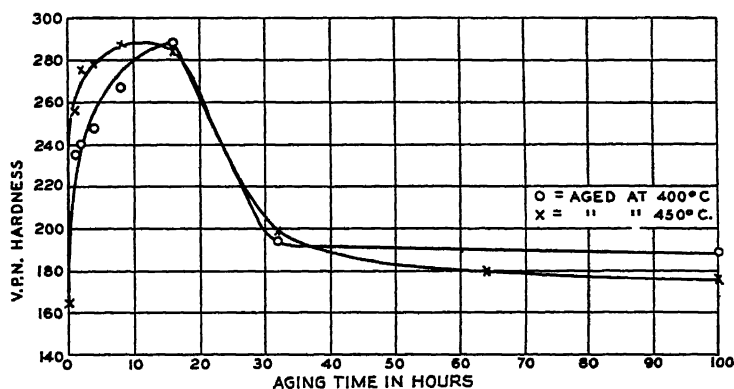


FIG. 6.—TIME-HARDNESS CURVE FOR ALLOY 2, CONTAINING 4.74 PER CENT TI.

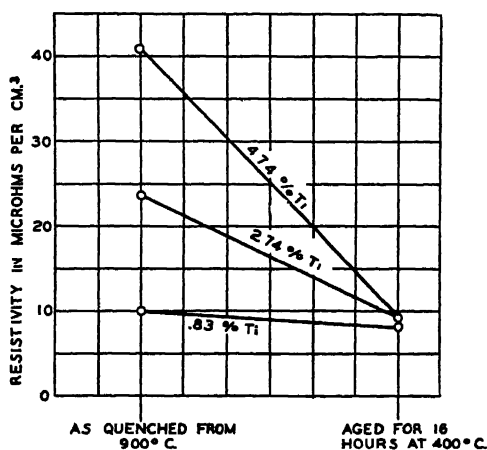


FIG. 7.—CHANGE IN ELECTRICAL RESISTIVITY DURING AGING OF COPPER-TITANIUM SAMPLES.

TABLE 4.—*Electrical Conductivity of Forged Samples*

Sample No.	Ti, Per Cent	Quenched from 900° C.		Aged 16 Hr. at 400° C.	
		Resistivity, Microhms Per Cu. Cm.	Conductivity, Per Cent (Cu = 100 Per Cent)	Resistivity, Microhms Per Cu. Cm.	Conductivity, Per Cent (Cu = 100 Per Cent)
0	0.83	10.12	17.37	8.255	21.5
1	2.74	23.6	7.48	9.077	19.6
2	4.74	40.94	4.53	9.062	19.66

TABLE 5.—*Typical Tensile Properties*

Sample No.	Ti, Per Cent	Treat-ment	Proportional Limit, Lb. per Sq. in.	Yield Point, Lb. per Sq. in.	Tensile Strength, Lb. per Sq. in.	Elongation, Per Cent on 2 in.	Reduction, Per Cent	Brinell Hardness
X	2.58	a	10,000	21,200	54,000	37.7	46	
		b	26,000	82,000	104,100	16.7	36	
96	1.5	a	3,500	12,500	41,600	48.5	60.3	63
		c	40,000	52,700	80,500	31.5	49.5	148
		c	34,500	52,400	80,150	31.5	50.0	146
95	2.90	a	5,600	23,300	58,500	42	44	93
		c	49,000	75,000	104,300	20.0	20.0	200
		c	51,000	77,000	104,500	21.5	20.5	201

<sup>a</sup> As quenched from 900° C

<sup>b</sup> Quenched from 900° C and aged for 8 hr. at 450° C.

<sup>c</sup> Quenched from 900° C. and aged for 16 hr. at 400° C.

the resistivity of the alloys with a titanium content varying from 0.83 to 4.74 per cent is practically the same after aging at 400° C. This indicates that the solid solubility of titanium in copper at 400° C. cannot be much higher than 1 per cent. The rest of the titanium is precipitated as a titanium-copper compound, or possibly as pure titanium. The total resistivity, therefore, is inversely proportional to the sum of the conductivity of the solid solution of 1 per cent Ti plus the conductivity of the balance of the mixture, which does not amount to much.

*Tensile Data.*—Typical tensile properties as determined on forged and heat-treated samples are given in Table 5. The diameter of the test section of sample X was 0.250 in., while specimens 95 and 96 had standard dimensions; that is, 2-in. gage length and 0.505-in. diameter.

The age-hardening effects produced by the addition to copper of small amounts of titanium produce a large increase of the tensile properties. The proportional limit and the yield point are raised in some cases as much as 1000 per cent, while the increase in hardness amounts to only 100 per cent. The increase in tensile strength is directly proportional to the increase of hardness and the decrease of elongation, but the elongation values are still high enough to make the alloy very desirable as a structural material.

## DISCUSSION

(*Norman B. Pilling presiding*)

P. G. McVETTER, Pittsburgh, Pa. (written discussion).—The authors have presented some very interesting data on the changes in properties of certain alloys during long exposure to elevated temperatures. It is of interest to consider the effects of such changes upon alloys which are, in service, subjected to stress at elevated temperatures over long periods of time. The importance of this subject is indicated by the fact that

austenitic steels show very similar aging characteristics and many of them are being used where "creep" must be considered.

Table 5 shows the large increase in strength and corresponding decrease in ductility resulting from aging treatments. Assuming that changes in hardness give a fairly accurate indication of changes in strength, the effects of aging at various temperatures are shown in Fig. 5 and Table 3. As the aging temperature is decreased, the time required to reach maximum strength is greatly increased. For example, the time increases from 7 hr. at 450° C. to 16 hr. at 400° C., and to more than 100 hr. at 350° C. Since the strength decreases from its maximum value as a result of continued heating at 400° and 450° C., it is reasonable to suppose that a similar action takes place at a slower rate at lower temperatures with an ultimate reduction in strength to a value approximating that found prior to the aging treatment.

When creep tests are made on an alloy having age-hardening properties, the measured creep rate is influenced by the strengthening effect of this hardening. If the temperature is such that the maximum aging effect is not reached during the test, we may expect an increasing creep rate to occur in service when the strength begins to decrease after the maximum value has been passed.

Within the range of alloys covered by the authors in this paper, the decrease in ductility is not serious. In other alloys which are hardened by precipitation, the ductility may be reduced to a very low value. This possibility that the material may become brittle in service is sufficient to prevent the use of such alloys in many high-temperature applications.

The question of stability in service cannot be overlooked, especially in high-temperature applications where ductility is important or deformation must be held within close limits.

E. E. SCHUMACHER and W. C. ELLIS, New York, N. Y. (written discussion).—Several years ago, in the course of a general survey of age-hardening systems of copper, we investigated the copper-rich copper-titanium alloys. Some months ago, certain of the data that were collected in this investigation were submitted to *Metals & Alloys* for publication.<sup>4</sup> Even though these data are available, it seems of value to mention at this time a few of the results that were obtained, because the titanium we used in preparing our alloys was of a higher purity than that used by the present authors. This is particularly pertinent in view of the fact that iron and silicon, which were present in appreciable quantities in the titanium used by Hensel and Larsen, form, with copper, a system with a variable alpha range.

The titanium used in our work was prepared by the reduction of the chloride with sodium and was of high purity, well over 99.5 per cent Ti. A spectrographic analysis showed only traces of iron, silicon, magnesium, copper and calcium.

The results of an investigation with alloys prepared from pure materials confirm the age-hardening characteristics reported by the present authors. These copper-titanium alloys, however, are difficult to prepare, because of the formation of high-melting constituents in the liquid melt, resulting in slushy metal and nonhomogeneous castings. This condition probably is due, as mentioned on page 55, to the absorption of constituents from the air. The necessity for careful melting methods is a decided disadvantage in the production of large quantities of metal. We did not find the physical properties better than those of the age-hardening copper-nickel-silicon alloys prepared under ordinary melting conditions.

D. K. CRAMPTON, Waterbury, Conn.—I was much interested in the results reported in this paper, particularly the physical properties given in Table 5, which show a good combination of tensile strength, elongation and reduction of area. In this connection,

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<sup>4</sup> E. E. Schumacher and W. C. Ellis: Age-hardening of Copper-titanium Alloys. *Metals & Alloys* (1931) 2, 111.



although I do not wish to be hypercritical, I do not think it is correct to refer to a percentage increase in hardness, as is done in the last paragraph of the paper. It is true that there is a 100 per cent increase in *hardness number*, but that is not the same thing as a 100 per cent increase in hardness, as the hardness scale is purely empirical.

Solid solubility as determined from the conductivity relationships is also referred to on page 62. The statement is made, "This indicates that the solid solubility of titanium in copper at 400° C. cannot be much higher than 1 per cent." If that statement is based solely on the conductivity data submitted, I would consider it better to say that the conductivity at that temperature was somewhat less than 0.83 per cent, as obviously the 0.83 per cent Ti is not all held in solution at that temperature.

Pure copper heated in an oxidizing atmosphere at 900° C. oxidizes rapidly and scales heavily. Did the author notice any particular difference between these alloys and pure copper in that respect, and also the rate of oxidation of the alloys on reheating at the aging temperature?

F. R. HENSEL (written discussion).—Mr. McVetty's remarks regarding the effect of age-hardening on creep brings up a question which should be carefully studied before age-hardening alloys are put in service at elevated temperatures. The problem becomes especially serious if by aging the ductility is decreased to low values. Fortunately this is not the case with copper-titanium alloys. The elongation values after aging remain extremely high.

We are sorry not to have known of the investigation by Schumacher and Ellis before this paper was written. It is gratifying, however, to learn that in general their results agree with ours. It may be of interest to give here (Table 6) a comparison of the physical properties of copper-titanium alloys as compared with the Corson alloys.<sup>5</sup>

TABLE 6.—*Physical Properties of Copper-titanium Alloys Compared with Those of Corson Alloys*

Material	Prop. Limit, Lb. per Sq. In.	Yield Point, Lb. per Sq. In.	Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent	Brinell Hardness	Electrical Resistivity, Microhms per Cu. Cm.
Cu-Ti alloy (1.5 per cent Ti)...	40,000	52,400	80,150	31.5	148	8
Corson alloy with 2 per cent Ni <sub>3</sub> Si.....	22,000	40,000	64,000	28	128	2.8
Cu-Ti alloy (2.9 per cent Ti)...	51,000	77,000	104,500	21.5	238	9.07
Corson alloy with 4 per cent Ni <sub>3</sub> Si.....	40,000	74,000	106,000	18	178	3.1

The tensile properties of the alloys compare very favorably with the Corson alloys. The principal disadvantage of the titanium alloys is the fact that their resistivity is three times that of the comparable Corson alloys.

As compared with the best complex high-strength brasses,<sup>6</sup> the titanium alloys are superior in elastic and electrical properties. In reply to Mr. Crampton's last question, I cannot give any quantitative information on the oxidation characteristics, but the difference in this respect between pure copper and copper-titanium alloys containing less than 5 per cent Ti seemed to be only slight.

<sup>5</sup> M. G. Corson: Copper Alloy Systems with Variable Alpha Range and Their Use in the Hardening of Copper. *Proc. Inst. Metals Div., A.I.M.E.* (1927) 435.

<sup>6</sup> O. W. Ellis: High-strength Brasses. *Trans. A.I.M.E., Inst. Metals Div.* (1929) 508.

## Copper-beryllium "Bronzes"

By J. KENT SMITH,\* NEW YORK, N. Y.

(New York Meeting, February, 1932)

THE object of this investigation was to ascertain the effect of varying percentages of beryllium upon pure copper and the properties of the resultant alloys in their softest condition, the effect of heat hardening on them, and the extents to which these properties could be augmented by different combinations of heat hardening and cold rolling. The data compiled in this paper represent partial results of continuing work done by the writer during the years 1930 and 1931, which was a continuation of the unpublished ground work incepted in the laboratory of the Beryllium Corporation of America by H. B. Pulsifer in the year 1926. A short bibliography on beryllium alloys is appended to this paper.

It has, of course, long been known that copper subjected to cold work is hardened and strengthened to a considerable extent; furthermore it had been qualitatively noted in previous experiments that copper-beryllium alloys seemed to take on hardness and strength as the result of cold work at a greater rate even than does plain copper. It was decided therefore to endeavor quantitatively to determine such rate of increase, as also the relative increases by combinations of cold working and heat hardening. The results are summarized in Tables 3, 4 and 5.

A preliminary series of experiments had indicated that by an exposure to the heat of 575° F. for 2½ hr. age-hardening of a 2.50 per cent beryllium-copper alloy took place.

Slab ingots of nine different beryllium-copper alloys were prepared under identical conditions by means of the addition of a previously prepared 12.5 per cent beryllium-copper alloy to well melted and deoxidized pure copper. The ingots were then reduced by hot rolling to 12 gage (about 0.080 in.). These strips were heated to 1450° F. and quenched in cold water, and thus brought to their softest condition. (See Table 1.) Strips were next "precipitation-hardened" by reheating to a definite temperature. Similar strips to those itemized in Table 1 (which had been quenched from 1450° F.) were reheated for varying periods of time at 575° F. The hardness figures show that a metastable condition, of which the range of stability is dependent entirely upon time at the given temperature, begins to be noted in copper samples containing as little as 0.85 per cent beryllium. It is extremely noticeable in samples containing

\* Consulting Metallurgist, Beryllium Development Corporation.

TABLE 1.—*Physical Properties of Beryllium Bronzes That Have Been Hot Rolled, Heated to 1450° F. and Quenched in Cold Water*

Sample No	Specific Gravity	Be, Per Cent	Tensile Strength, Lib per Sq In	Elongation, Per Cent in 2 In	Hardness of Strip, <sup>a</sup> Rockwell B	Fig. No.	Hardness of Original Cast Ingot, <sup>a</sup> Rockwell B
Pure copper	8.89	0	32,600	42.5	23 $\frac{1}{2}$	1	
1	8.78	0.34	42,500	46.5	27 $\frac{1}{2}$	2a	32 $\frac{1}{2}$
2	8.61	0.87	50,200	42.5	37 $\frac{1}{2}$		36
3	8.48	1.24	55,700	48.0	43 $\frac{1}{2}$		49 $\frac{1}{2}$
4	8.43	1.36	57,100	52.5	52 $\frac{1}{2}$	3a	52 $\frac{1}{2}$
5	8.34	1.68	62,000	55.0	53 $\frac{1}{2}$		60 $\frac{1}{2}$
6	8.28	1.91	65,600	59.0	55 $\frac{1}{2}$		67
7	8.20	2.20	75,500	50.0	60 $\frac{1}{2}$	4a	74
8	8.11	2.51	84,000	32.5	64 $\frac{1}{2}$	5a	
9	8.04	2.75	88,800	29.0	66 $\frac{1}{2}$		

<sup>a</sup> Note that the Rockwell ingot hardness on samples 1 to 4 agrees well with the softened strip hardness but that at the point where age-hardening becomes perceptible in the alloy as subsequently noted the ingot hardness begins to diverge from the softened strip hardness.

FIG. 1.—PURE COPPER. ETCHED, VERTICALLY ILLUMINATED.  $\times 500$ .

about 1.5 per cent beryllium, and continues to exist (though in decreasing intensity) in samples containing up to nearly 2 per cent of beryllium, after which an approximate constant is quickly reached irrespective of prolonged time. (See Table 2.)

TABLE 2.—*Physical Properties of Copper-beryllium Alloys As Quenched from 1450° F. in H<sub>2</sub>O and Reheated to 575° F.*

Sample No	Be, Per Cent	Tensile Strength, Lb per Sq In 3-hr. Draw	Elongation, Per Cent in 2 In.	Rockwell B Hardness after Reheating to 575° F. for			Fig No.
				3 Hr.	7 Hr.	24 Hr.	
Pure copper	0	32,000	46.5	2½ <sub>5</sub>	2½ <sub>5</sub>	2½ <sub>5</sub>	
1	0.34	42,500	46.5	3½ <sub>3</sub>	3½ <sub>3</sub>	3½ <sub>3</sub>	
2	0.87	49,000	42.5	3½ <sub>6</sub>	3½ <sub>40</sub>	4½ <sub>48</sub>	2b
3	1.24	57,700	48.5	4½ <sub>0</sub>	5½ <sub>3</sub>	6½ <sub>1</sub>	
4	1.36	60,500	46.0	5½ <sub>5</sub>	5½ <sub>6</sub>	8½ <sub>4</sub>	
5	1.68	76,200 <sup>a</sup>	30.0	5½ <sub>2</sub> <sup>a</sup>	8½ <sub>1</sub>	10½ <sub>101</sub> <sup>b</sup>	3b <sup>a</sup>
		127,100 <sup>b</sup>	14.5				
6	1.91	147,000	11.0	10½ <sub>104</sub>	10½ <sub>106</sub>	10½ <sub>106</sub>	
7	2.20	154,000	8.5	10½ <sub>107</sub>	10½ <sub>107</sub>	10½ <sub>108</sub>	4b
8	2.51	155,000	7.5	10½ <sub>109</sub>	10½ <sub>109</sub>	10½ <sub>109</sub>	
9	2.75	161,000	5.0	10½ <sub>110</sub>	10½ <sub>110</sub>	10½ <sub>110</sub>	5b

<sup>a</sup> Drawn 3 hr. as other tensile samples.

<sup>b</sup> Sample drawn 24 hours.

While it was attempted to reduce by cold work all the samples that had been hot-rolled by three further constant amounts (50, 75 and 90 per cent respectively), samples 7, 8 and 9 became so intensely resistant to the reducing action of the rolls that it was possible, for purely mechanical reasons, to reduce these by only 80 per cent or less in the final rolling instead of the 90 per cent desired.

It was obviously impossible to take the hardness of very thin material by the Rockwell method, therefore hardness readings were made on the Monotron. For the purposes of rough comparison, some observed Rockwell B/16 hardnesses read on 0.040-in. sheets (which were obviously approximate only in their correctness) against observed Monotron figures on the same sheets give the results shown below.

ROCKWELL B HARDNESS <sup>a</sup>	MONOTRON HARDNESS	ROCKWELL B HARDNESS <sup>a</sup>	MONOTRON HARDNESS
81	140	100	190 <sup>a</sup>
90	170	101½	215
98	185	102½	225
99	190	106	275

<sup>a</sup> Measurements of Rockwell as noted above on this thickness are naturally subject to considerable error.

TABLE 3.—Effect of Cold-rolling Strips of Table 1 without Further Heat Treatment

Sam- ple No.	Be, Per Cent	Reduced 50 Per Cent			Reduced 75 Per Cent			Reduced 90 Per Cent		
		Tensile Strength, Lb. per Sq. In.	Elongation, Per Cent in 2 In.	Monotron Hardness <sup>a</sup>	Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>	Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>
0	0	See Table 5								
1	0.34	74,900	3.00	140	93,000	2.50	152	105,000	1.00	160
2	0.87	97,600	3.00	165	117,000	2.00	172	142,200	1.00	195
3	1.24	114,100	2.75	185	140,000	2.00	200	160,000	1.00	205
4	1.36	120,000	3.00	185	144,000	1.75	208	167,000	1.00	210
5	1.68	123,400	2.05	190	152,800	2.00	220	176,500	1.00	230
6	1.91	132,300	3.00	215	158,000	1.50	230	177,400	1.00	235
7	2.20	139,200	3.00	225	162,000	1.50	240	188,000 <sup>b</sup>	1.00	240
8	2.51	147,600	3.00	255	169,010	1.50	262	210,000 <sup>b</sup>	1.00	265
9	2.75	155,000	3.00	260	176,000	1.50	265	197,140 <sup>b</sup>	1.00	265

<sup>a</sup> For relation to Rockwell hardness see page 67.<sup>b</sup> Not fully reduced.

TABLE 4.—*Effect of Heat-hardening the Cold-rolled Strips of Table 3*

Sam- ple No	Be, Per Cent	Reduced 50 Per Cent			Observed Rockwell B Hardness (Approx.)	Reduced 75 Per Cent			Reduced 90 Per Cent		
		Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>		Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>	Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>
0	0	32,000	Not taken	Not taken	2 9/28	48,000	Not taken	Not taken	61,600	Not taken	Not taken
1	0.34										
2	0.87	97,000	16.0	170	8 9/11	117,000	12.0	172	122,500	8.5	192
3	1.24										
4	1.36	126,600	11.0	172	10 2/103	129,000	9.0	182	141,200	5.0	212
5	1.68										
6	1.91										
7	2.20	156,800	6.5	242	10 9/110	163,100	2.5	253	183,000 <sup>b</sup>	1.5	263
8	2.51	167,800	3.5	263		182,000	1.5	270	211,000 <sup>b</sup>	1.0	270
9	2.75	214,000	1.0	283		225,800	1.00	300	230,000 <sup>b</sup>	1.0	303

<sup>a</sup> For relation to Rockwell hardness see page 67.<sup>b</sup> Not fully reduced.



FIG. 2.—BERYLLIUM BRONZE; 0.87 PER CENT BE. ETCHED, VERTICALLY ILLUMINATED.  $\times 500$ .

a. Soft. b. Age-hardened.



FIG. 3.—BERYLLIUM BRONZE; 1.68 PER CENT BE. ETCHED, VERTICALLY ILLUMINATED.  $\times 500$ .  
*a.* Soft. *b.* Age-hardened.





FIG. 4.—BERYLLIUM BRONZE; 2.20 PER CENT BE. ETCHED, VERTICALLY ILLUMINATED.  $\times 500$ .  
*a.* Soft. *b.* Age-hardened.

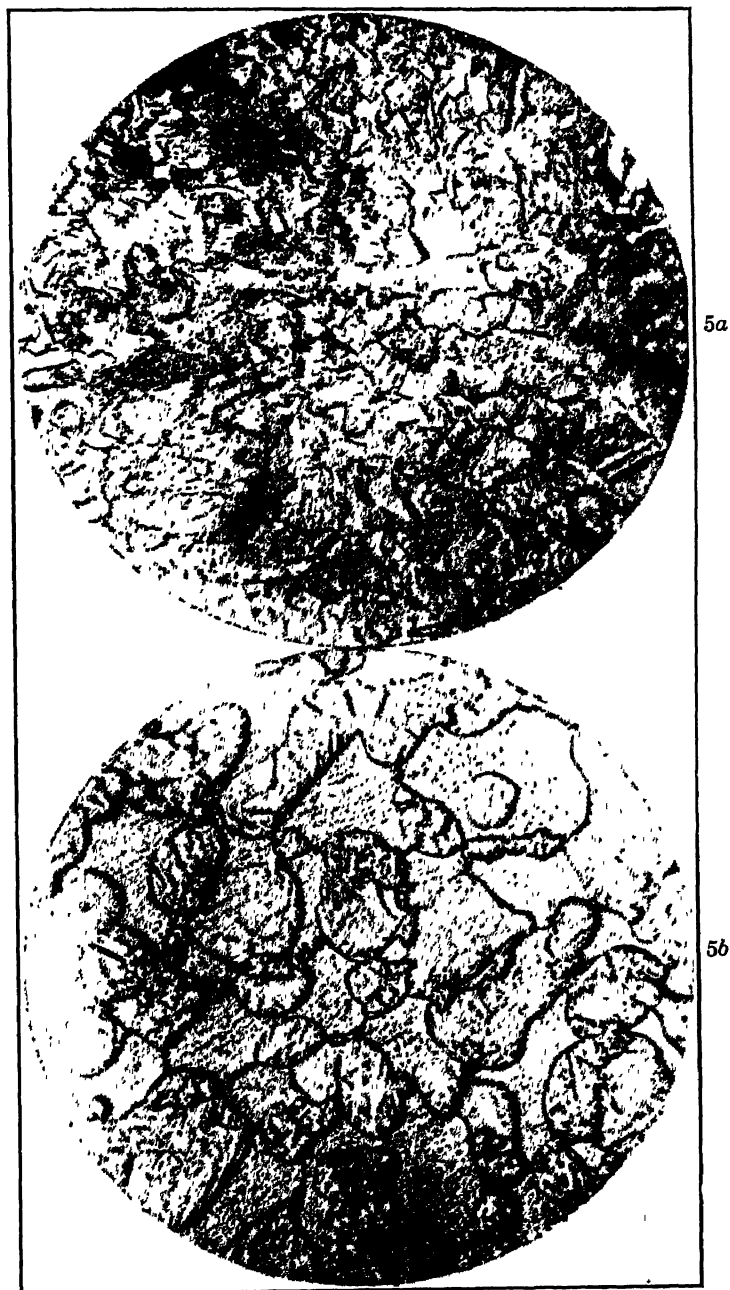


FIG. 5.—BERYLLIUM BRONZE; 2.75 PER CENT BE. ETCHED, VERTICALLY ILLUMINATED.  $\times 500$ .  
*a.* Soft. *b.* Age-hardened.

The hot-rolled strips were softened by quenching from 1450° F., then reduced by cold-rolling 50, 75 and 90 per cent respectively, and in each case the resultant rolled product heated at 575° F. for 7 hr. (See Table 4.) No attempt was made to explore the time-temperature ratio which would be expected to exist to some modified degree in the case of sample 5, as evidenced by the results itemized in Table 2.

Representative hot-rolled 12-gage strips were softened by quenching at 1450° F., heat-hardened at 575° F. for 7 hr. and subsequently reduced by cold rolling to 50, 75 and 90 per cent respectively (Table 5).

From the foregoing several facts emerge. Perhaps the most noteworthy, in addition to the specific notes already made as to the effect of time and temperature on the transformation of alloys in the metastable zone, are the strikingly increased rates at which copper-beryllium bronzes harden and strengthen by cold work in comparison with pure copper, and the attainment of a tensile strength as high as 220,000 lb. from a copper-beryllium alloy containing only 1.91 per cent beryllium and 98.09 per cent of copper by softening, heat-hardening, and *then* cold-rolling a plate.

The previous figures all refer to wrought materials, but a large number of individual trials have proved that by age-hardening simple copper-beryllium castings of the same compositions about 80 per cent of the augmented strength and hardness figures shown in Tables 1 and 2 are attained.

The possibility of hardening plates after their formation in soft condition is amply demonstrated, as also the extreme adaptability of the copper-beryllium alloys containing 2.50 per cent beryllium or more for the preparation of gears which are required to work in corrosive conditions, without deformation in their hardening.

Beryllium-copper in the form of a master alloy containing 12 to 15 per cent metallic beryllium and the remainder copper, and of a specific gravity approximating 6.0, is now available both for commercial and further experimental work. In using this alloy to prepare the various beryllium bronzes, the procedure is very simple. The copper charge is dead melted under a simple flux and/or covering of charcoal, according to the shop practice of the user. The bath of molten metal is then superheated about 200° F. above pouring temperature, the broken master alloy added and quickly stirred in with a graphite, plumbago, or other suitable stirring rod, taking care that the alloy is not left floating on the top of the crucible and thus exposed to the furnace atmosphere. The whole is then allowed to come—either by heating or by further cooling as the case may be—to the pouring temperature proper for molten copper, and subsequent casting operations are performed as usual.

Particular care should be taken that in the subsequent fabrication of the alloy the temperature never is allowed to exceed 1475° F. in commercial or other practice, as otherwise the metal will "burn"

TABLE 5.—*Effect of Cold-rolling the Heat-hardened Strips of Table 2*

Sam- ple No	Re- cent	Reduced 50 Per Cent			Observed Rockwell B Hardness (Approx.)	Reduced 75 Per Cent			Reduced 90 Per Cent		
		Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>		Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>	Tensile Strength, Lb. per Sq. In.	Elongation Per Cent in 2 In.	Monotron Hardness <sup>a</sup>
1	0.34	77,000	4.5	128	77 $\frac{1}{2}$	94,000	2.5	130	110,000	1.5	148
2	0.87										
3	1.24	123,500	4.5	190	98 $\frac{1}{100}$	148,100	2.5	213	176,000	1.5	225
4	1.36										
5	1.68										
6	1.91	171,600	3.5	275	108 $\frac{1}{108}$	199,000	1.5	280	220,700	1.5	285
7	2.20										
8	2.51	Not taken		290	Not taken						
9	2.75	Not taken		300	Not taken						

<sup>a</sup> For relation to Rockwell hardness see page 67.Too strong for equipment to ex-  
ercise cold reduction much above  
the 75 per cent. reported

and the proper results will not be obtained in the "precipitation-hardened" article.

#### ACKNOWLEDGMENTS

In conclusion the writer wishes cordially to thank the Beryllium Development Corporation and its staff for putting at his disposal the facilities which rendered possible this communication, and to Mr. Charles H. Monroe for valued help.

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#### DISCUSSION

(John R. Freeman, Jr., presiding)

C. H. GREENALL, New York, N. Y.—The statement made by Mr. Smith as to the impossibility of taking Rockwell hardness readings on thin sheet metals below 0.040 in. has not been the experience of the Bell Telephone system. During the past five years purchases of material 0.020 in. thick have been made successfully, using the Rockwell hardness tester. It was necessary to develop a new Rockwell hardness scale for materials of a hardness approaching that of phosphor bronze and beryllium copper. This scale made use of the 150-kg. load,  $\frac{1}{16}$ -in. ball penetrator, reading the red figures, or B scale. This scale, with the method of standardizing the Rockwell machine, as used in the Bell system, has given satisfactory results to both the suppliers and consumers of nickel silver and phosphor bronze. Data on our experience were presented before the American Society for Testing Materials in two papers prepared jointly by the American Brass Co., the Western Electric Co. and the Bell Telephone Laboratories.<sup>1</sup>

<sup>1</sup> H. N. Van Deusen, L. I. Shaw and C. H. Davis: Physical Properties and Methods of Test for High Sheet Brass. *Proc. Amer. Soc. Test. Mat.* (1927) **27**, II, 173.

J. R. Townsend, W. A. Straw and C. H. Davis: Physical Properties and Methods of Test for Some Sheet Nonferrous Metals. *Ibid.* (1929) **29**, 381.

O. W. ELLIS, Toronto, Ont.—There is one point that I think should not be overlooked. A number of alloys have been investigated which have shown excellent electrical conductivity and have appeared, therefore, to be quite satisfactory from the point of view of the electrical industry. But in certain cases those alloys have been deficient in heat conductivity, and heat conductivity, in so far as large electrical machines are concerned, is almost as important as electrical conductivity. I feel that in any investigation that Mr. Smith may make on the conductivities of these alloys the heat as well as the electrical conductivity should be considered.

## Some Developments in High-temperature Alloys in the Nickel-cobalt-iron System

By C. R. AUSTIN\* AND G. P. HALLIWELL,† PITTSBURGH, PA.

(Boston Meeting, September, 1931)

THE investigation described in this paper deals with the development of high-temperature alloys of the Konel series over a considerable period of time at the Research Laboratories of the Westinghouse Electric and Manufacturing Co. The word "Konel" has been coined to designate a class of alloys which are essentially nickel-cobalt-iron with other elements added, usually in small quantities. Most of these alloys contain titanium, usually about 2.5 per cent. The main consideration related to strength at high temperatures but the thermionic characteristics of the alloys was also of considerable importance. It is, however, with the mechanical properties at elevated temperatures that we are herein concerned. Much attention has also been devoted to their age-hardening characteristics.

There is little need to stress the utilitarian aspect of this subject, as it has been discussed frequently. Alloys exhibiting superior properties at normal or elevated temperatures rapidly find many suitable applications. There may be some question, however, as to what constitutes a "superior alloy," or an alloy that may have good service possibilities at high temperatures. The problem is complex and various means have been employed to predict the useful life that may be expected of a material. In recent years the "creep limit" has been used as the best means of evaluation. Such tests necessarily are prolonged and hence collection of data is very slow. In a general survey of many alloys therefore the creep test is not desirable and recourse must be had to much shorter time tests in order more rapidly to select alloys which appear to show promise. For this reason the present survey has been made using the high-temperature tensile test and a bend test developed by Howard Scott.<sup>1</sup> In the tensile test the conditions have been standardized for all tests, so that values obtained are at least comparable, one alloy with another, although the absolute values recorded merely indicate the mechanical properties at the given temperature under a definite rate of loading.

\* Research Laboratories, Westinghouse Elec. & Mfg. Co.

† Carnegie Institute of Technology.

<sup>1</sup> H. Scott: High Temperature Characteristics of Metals Revealed by Bending. *Proc. Amer. Soc. Test. Mat.* (1931).

No attempt will be made to review the previous literature on the subject, as many bibliographies are available, but reference must be made to a recent paper by Clark and White,<sup>2</sup> which includes Konel metal in the group of alloys tested. These authors concluded that Konel had the highest recrystallization temperature of the series, as revealed by hardness measurements. From this they inferred that the Konel metal would have the best creep properties. This deduction was experimentally confirmed. The word "Konel" has been used frequently by Clark and White to indicate a specific alloy in this series which has found successful commercial application as a base material for oxide-coated thermionic cathodes.<sup>3</sup>

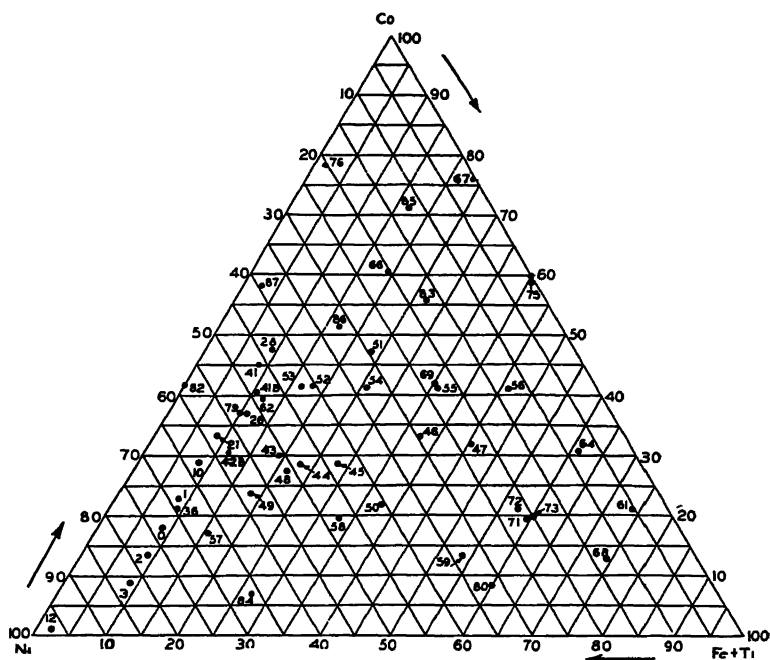


FIG. 1.—DISTRIBUTION OF ALLOYS CONSIDERED IN TERNARY SYSTEM Ni-Co-Fe-Ti. Iron-titanium in all these alloys contains sufficient titanium to yield about 2.5 per cent. in final alloy. Alloys 36, 41, 41B, 42B, 43 and 44 also contain chromium (Table 1).

### ALLOYS INVESTIGATED

All the alloys investigated may be considered as occupying some location in the nickel-cobalt-iron or nickel-cobalt-ferrotitanium ternary system and containing limited amounts of carbon with perhaps aluminum,

<sup>2</sup> C. L. Clark and A. E. White: Properties of Non-Ferrous Alloys at Elevated Temperatures. Amer. Soc. Mech. Engrs., *Advance Paper* 12 (1930).

<sup>3</sup> E. F. Lowry: The Role of the Core Metal in Oxide Coated Filaments. *Phys. Rev.* (1930) **35**, 1367.



silicon and manganese added as deoxidizing agents. The ferrotitanium used was an alloy consisting of 75 per cent. iron and 25 per cent. titanium. Some of the alloys also contain chromium. About 100 alloys were examined with some degree of thoroughness and the composition of some of the most interesting can be illustrated best by reference to the conventional diagram representing a ternary system. All the alloys shown in Fig. 1 contain approximately 2.5 per cent. titanium. The low iron content of alloys 76, 82 and 87 made it necessary to add pure titanium in order to make up a 2.5 per cent. titanium content. Fig. 2 shows the composition of some interesting alloys wherein the titanium content did not approximate 2.5 per cent.

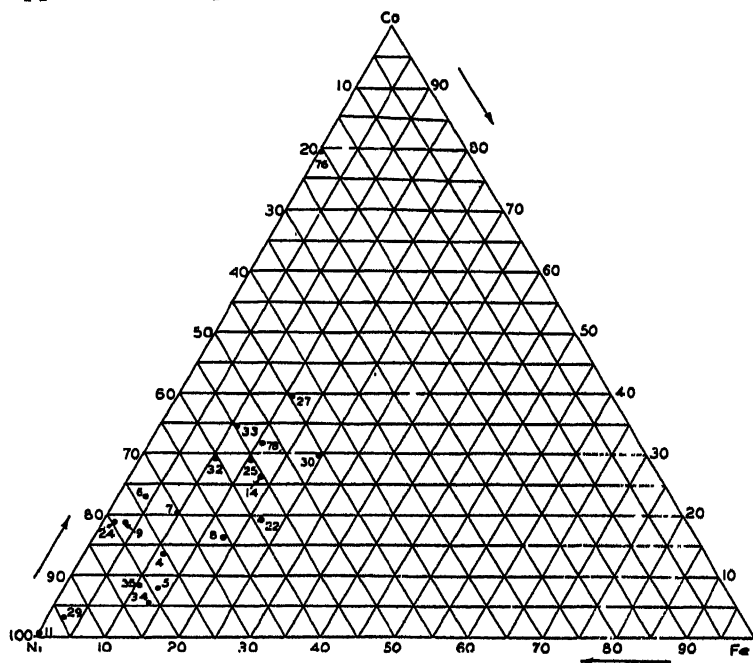


FIG. 2.—DISTRIBUTION OF ALLOYS CONSIDERED WHEREIN PERCENTAGE OF TITANIUM IS VARIABLE.

### APPARATUS AND PROCEDURE

The alloys were prepared in an induction furnace in 8-kg. melts and chill-cast as 2-in. square bars. The crucible consisted of pure magnesia, and the purest commercial metals were employed. The titanium occasionally was added as pure stick titanium, but usually as ferrotitanium because in the major portion of the alloys prepared the iron-titanium ratio was 3 to 1—the same as that in the ferrotitanium employed.

After casting the alloys the general procedure was as follows:

1. The alloys were homogenized at about 1000° C. for 8 hr. after packing in granular magnesium oxide and cooled in the air.

2. Machined or ground to remove all surface imperfections.
3. The ingots were then hot-forged to 1 or  $\frac{1}{2}$  in. square, with intermediate grinding wherever necessary to maintain a good surface.
4. Sections were cut for standard tensile test pieces, which were heat-treated as follows: (a) annealed 1 hr. at 950° C. and air-cooled; machined to tensile test size; (b) aged at 650° C. for 72 hr. in vacuum and quenched in water. The material was then ready for test.
5. Sections were cut for aging different periods of time at different temperatures and examining effects by means of Vickers hardness numbers.
6. Sections were prepared for elastic bend test by rolling down to final size.

The mechanical tests at high temperature were of the conventional type, the heating of the specimen being effected by use of a "nichrome" wound furnace. All these high-temperature tests were conducted at 600° C. The physical properties at normal temperature were also measured for purposes of comparison.

The bend test has recently been fully described,<sup>4</sup> so that no analysis of the test is attempted here. The test, however, may be described as a novel method by means of which the degree of plastic deformation in a metal strip loaded by bending is evaluated in terms of the maximum strain applied. From the variation of this property with maximum strain and with time, properties equivalent to the tensile proportional limit and creep limit respectively may be determined. Also a limited temperature range, about which the metal (begins to lose all its elastic property) is recognized. The value of this test lies in the fact that these properties can be determined quickly.

#### EXPERIMENTAL RESULTS

The most convenient method of presenting and discussing the results obtained will be effected by considering the data under the following subheadings:

1. Mechanical properties of the alloys.
2. Aging characteristics as revealed by various time-temperature observations on the Vickers hardness.
3. Bend-test description and observations.

#### MECHANICAL PROPERTIES OF THE ALLOYS

The details of the method of high-temperature testing as applied to the present alloys have been fully described in a paper by Lynch, Mochel and McVetty.<sup>5</sup>

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<sup>4</sup> H. Scott: *Op. cit.*

<sup>5</sup> T. D. Lynch, N. L. Mochel and P. G. McVetty: Tensile Properties of Metals at High Temperatures. *Proc. Amer. Soc. Test. Mat.* (1925) 25, Pt. 2, 5.

The Johnson limit, proportional limit, elongation, reduction in area and tensile strength were evaluated at 600° C. and at room temperature on almost all the alloys. In the earlier stages of the work some of the high-temperature tests showed erratic results when the alloys were air-cooled following annealing. This was found to be due to a variation in the amount of age-hardening which occurred in raising the alloy to the temperature of test and maintaining until quasi-equilibrium conditions were obtained. All alloys, therefore, were subjected to age-hardening before testing. This aging was preceded by annealing for 1 hr. at 950° C. and was followed by a water quench. After machining to finished size, the tensile test pieces were aged for 72 hr. at 650° C. in a vacuum. Some of the most interesting results have been tabulated and are presented in Tables 1 and 2. Table 1 includes alloys that have not been aged before testing; all alloys in Table 2 have been aged as indicated. It is desired to focus attention more particularly on the aged alloys and the examples selected were taken from the accumulated data, which showed a minimum of about 5 per cent. elongation in 2 in. A few examples exhibiting practically no elongation but rather strikingly high values for the proportional limit at 600° C. have also been included.

Complete physical data of the tests were recorded in file but only a limited number have been included, for the sake of brevity. Greatest significance has been given to the values representing proportional limit, as it is believed that this property is the best index obtained from high-temperature mechanical test data of resistance to creep. Elongation and reduction in area are important in checking the ductility of the alloys. The tensile strength is added more for the purpose of correlating with other available high-temperature test data. The addition of room-temperature values permits an analysis of the effect of elevating the temperature, on the various physical properties considered.

No creep values have been obtained on any of these alloys, but it would seem from the high values for proportional limit obtained with a few of the materials that an examination of creep stresses is desirable.

It is difficult to cull examples from the literature to serve as a comparison basis for these alloys. Few data on high-temperature aging are available and the mechanical properties obtained depend so much on factors such as temperature of test and rate of testing that a true comparison is difficult. Hatfield<sup>6</sup> cites the results of tests at 800° C., but this temperature shows too great a temperature difference from that of our own tests to make comparison worth while. A few data on tensile

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<sup>6</sup> W. H. Hatfield: The Application of Science to the Steel Industry, 124. Campbell Memorial Lecture, Amer. Soc. Steel Treat. Evangelical Pub. House, Cleveland, 1928.

TABLE 1.—*Chemical Composition and Some Physical Test Data on Several Alloys Examined*  
 Test Pieces Were Annealed at 950° C. and Furnace-cooled. No Subsequent Aging.

Alloy No.	Composition, Per Cent.					Proportional Limit, Lb. per Sq. In.		Yield Point, 0.2 Per Cent.		Tensile Strength, Lb. per Sq. In.		Elongation, Per Cent. in 2 In.		Reduction in Area, Per Cent.	
	Ni	Co	Fe	Ti	Ta or Zr	Room Temp.	600° C.	Room Temp.	600° C.	Room Temp.	600° C.	Room Temp.	600° C.	Room Temp.	600° C.
6	72.3	23.0	3.7	1.24		20,000	14,700	32,700	24,000	90,100	47,700	47.0	44.5	64.0	59.5
12	96.4	1.1	0.22	2.2		11,000	7,750	22,600	15,450	76,300	42,600	55.0	48.5	73.0	62.0
11	94.4	1.0	0.25	4.36		17,000	10,200	26,800	19,500	87,500	53,000	54.0	39.0	74.0	43.0
15	97.5		0.42		1.97 Ta	14,000	7,750	26,200	17,200	70,650	40,420	50.0	30.8	79.4	45.0
19	98.4		0.04		1.51 Zr	13,000	12,250	27,500	24,300	79,250	54,610	36.3	35.6	54.0	71.3
24	76.6	17.6	1.6	3.7		29,000	18,200	52,700	42,500	104,000	70,300	47.0	36.0	65.0	52.0
0*	73.8	17.3	6.25	2.22	(Konal)	20,000	20,500	30,500	27,600	93,100	65,970	50.5	25.0	69.0	28.0
2	76.8	13.6	6.3	2.4		21,000	14,000	35,700	26,300	97,000	61,000	41.0	23.0	66.0	26.0
3	82.0	8.5	6.3	2.3		19,000	13,500	32,300	26,500	92,700	59,500	51.0	21.0	69.0	27.6
16	93.4		0.95		5.14 Ta	24,000	11,750	34,300	20,400	87,150	54,800	40.6	27.3	70.5	38.1
21	57.9	33.1	6.34	2.53		19,900	32,300	30,100	57,400	92,000	91,800	51.5	20.0	68.0	22.6
26	51.8	35.5	8.7	2.7		36,000	33,750	50,800	53,000	104,500	91,200	37.3	22.5	63.3	25.0
28	43.1	46.3	6.87	2.9		26,000	31,500	42,300	55,000	105,000	90,900	36.5	22.5	59.1	24.7
0†	73.3	17.3	6.25	2.22	(Konal)	31,250	23,000	51,000	41,600	102,250	66,000	37.0	18.5	50.8	25.5
1	68.3	22.6	6.2	2.4		26,000	20,000	36,700	32,750	98,600	69,300	43.0	17.0	66.0	19.6
9	77.4	18.7	2.87	1.1		13,000	6,000	24,200	15,300	83,900	41,000	51.5	16.5	67.5	16.2
10	62.5	28.5	6.1	2.4		17,000	23,500	31,100	34,500	91,800	80,500	52.0	12.2	67.0	10.5
13	100					5,000	3,375	12,700	10,650	61,400	29,000	40.0	16.9	64.5	21.4
29	88.6	2.6	2.87	5.86		23,000	20,500	35,800	57,500	100,750	82,900	38.0	12.3	40.3	20.5

\* Air-cooled.

† Quenched after 23 hr. at 600° C.

TABLE 2.—*Chemical Composition and Some Physical Test Data on Several Alloys Examined*  
 Test Pieces Were Annealed at 950° C. and Quenched in Water, Then Aged at 650° C. for 72 Hours.

Alloy No	Composition, Per Cent.					Proportional Limit, Lb. per Sq. In.		Yield Point, 0.2 Per Cent.		Tensile Strength, Lb. per Sq. In.		Elongation, Per Cent. in 2 In.		Reduction in Area, Per Cent.	
	Ni	Co	Fe	Ti	Cr	Room Temp.	600° C.	Room Temp.	600° C.	Room Temp.	600° C.	Room Temp.	600° C.	Room Temp.	600° C.
0	73.3	17.3	6.25	2.4		27,500	15,000	58,000	46,800	108,000	76,800	35.0	24.7	59.5	33.2
21 <sup>a</sup>	57.9	33.1	6.34	2.58		45,000	52,000	83,600	81,600	137,100	105,000	35.0	24.7	59.5	33.2
42B	46.1	24.86	7.02	2.19	18.74	70,000	57,500	104,000	86,000	164,750	127,100	29.0	21.5	37.0	21.7
41	46.96	29.47	6.50	2.35	13.7	61,250	66,250		97,600		120,200		11.0		16.5
41B	48.9	29.50	8.4	2.4	9.46	52,500	52,500	99,000	87,400	160,500	121,500	27.0	11.0	43.0	14.1
55	22.86	40.38	34.04	2.23		57,500	37,500	99,500	89,500	145,000	107,700	18.0	11.0	42.0	16.0
69	23.19	39.94	33.4	2.24		50,000	32,500	100,000	78,000	135,000	103,100	17.6	11.1	43.5	20.4
43	50.98	28.66	15.5	3.14	1.14	72,500	41,200	109,000	97,150	159,000	119,500	12.0	5.0	15.6	10.0
44	48.3	27.34	19.97	2.71	0.34	80,000	57,600	105,200	97,200	170,250	121,000	26.0	5.2	43.0	10.6
51	28.93	19.73	44.70	2.39		67,500	44,000	123,500	90,000	157,700	113,500	16.3	6.5	46.3	9.8
62 <sup>b</sup>	48.06	29.28	9.42	2.72		80,000	48,700	114,500	97,000	168,000	119,000	23.6	6.5	41.6	17.0
54	32.98	40.23	23.95	2.19		72,000	45,000	97,200	89,500	154,500	111,000	19.3	4.8	41.3	6.7
57	67.6	14.64	14.52	2.5		65,000	46,200	92,000	81,400	156,700	92,000	28.6	2.3	38.0	11.0
58	47.7	15.64	33.52	2.21		55,000	37,200	103,000	86,500	149,000	112,500	28.6	2.3	38.0	10.5
52	40.15	40.93	15.85	2.44		80,000	37,800	114,000	105,000	170,000	130,500	22.0	4.1	44.6	9.3
66	20.53	58.64	17.44	2.46		70,000	42,500	103,000	89,100	149,500	119,000	21.3	9.6	49.3	13.6
61	5.07	19.05	72.44	2.61		95,000	12,500	120,000	88,200	154,000	47,500		4.6	3.1	4.7
67	Trace	75.71	21.46	2.19		37,500	13,500	74,500	33,500	109,250	51,750	27.0	52.0	63.5	80.5
68 <sup>c</sup>	70.00		27.5	2.5		65,000	49,500	97,000	92,000	150,250	100,000	15.5	4.0	20.4	5.3
73 <sup>c</sup>	20.0	20.0	57.5	2.5		75,000	16,000	125,000	48,500	167,750	76,500	18.0	37.5	29.0	72.0

<sup>a</sup> Aged 100 hours.

<sup>b</sup> Molybdenum 10.4 per cent

<sup>c</sup> Synthetic composition.

strength and elongation on nickel-chromium and nickel-chromium-iron alloys from published work by one of the present authors may be cited.<sup>7</sup>

TABLE 3.—*Mechanical Properties of Certain Nickel-chromium and Nickel-chromium-iron Alloys*<sup>a</sup>

Alloy No.	Composition Per Cent				Tensile Strength, Lb. Per Sq. In.		Elongation Per Cent in 2 In.	
	Ni	Cr	Fe	C	Room Temp.	650° C.	Room Temp.	650° C.
1	90	10			136,000	55,700	17	19
2	70	30			153,100	105,000	27	
3	60	40			168,000	106,100	10.5	10
4	90	9.5		0.5	134,600	86,900	25	40
5	58.66	21.03	20.16		144,400	92,200	13	5
6	69.50	19.10	9.48		113,900	78,100	28	20
7		38.50	61.39		113,100	39,200	2	28
8		9.77	90.16	0.42	285,600	46,600	6.5	38
9	69.50	28.98		0.39	131,000	122,300	22.5	14.5
10	39.11	30.21	29.74	0.48	147,000	93,000	12.5	10

<sup>a</sup> Taken from published data on high-temperature alloys.

Comparing these values with those in Table 1, where no aging had been given the material, it is noted that apparently extremely good physical properties are exhibited by the former. Thus alloy 9 shows a tensile strength of 122,300 lb. accompanied by an elongation of 15 per cent. at 650° C., a temperature 50° C. higher than that employed in the tests considered in the present work. This 70:30 nickel chrome was one of the most promising forgeable alloys examined in the published work cited. This alloy also gave particularly good creep limit values and it is probable that the proportional limit would be correspondingly high. All alloys recorded in Table 1 have not been aged and show an elongation greater than 10 per cent. at 600° C. Thus alloy 26 with 33,750 lb. proportional limit has an elongation of 22.5 per cent. This compares with 23,000 lb. limit and 18.5 per cent. elongation in regular Konel metal at 600° C.

Alloys 21 and 28 show an almost equally marked superiority over Konel at this temperature. In each of these alloys the improvement in high-temperature physical properties was obtained by a replacement of some of the nickel in the alloy with cobalt. The iron-titanium remains approximately constant. The percentage of reduction in area is also very satisfactory, and the ultimate strength has a value a little above 90,000 and is not far from the tensile value observed at room temperature.

<sup>7</sup> C. H. M. Jenkins, H. J. Tapsell, C. R. Austin and W. P. Rees: Some Alloys for Use at High Temperatures. Nickel-chromium and Complex Iron-nickel-chromium Alloys. *Jnl. Iron and Steel Inst.* (1930) 121, 237.

It must be remembered that on account of lack of preaging, all alloys in Table 1 have different amounts of aging, depending on the time taken to establish the temperature of test. As aging is fairly rapid, small differences in this time period are important. This point will be referred to again.

#### ALLOYS AGE-HARDENED BEFORE TESTING

Attention will now be given to the alloys that were age-hardened before testing, although more detailed consideration as to the aging characteristics will be given in the next section of the paper.

In the age-hardened alloys phenomenally high values for the proportional limit at 600° C. have been recorded. The highest of these is 66,250 for alloy 41, with an elongation of 11 per cent. This alloy contains 13.7 per cent. chromium. Alloy 44, which contains no chromium, has 57,500 lb. limit but only 5.2 per cent. elongation. Alloy 21, with 52,000 lb. limit, shows 25 per cent. elongation with good reduction of area. Alloy 66 shows 42,500 lb. proportional limit with almost 10 per cent. elongation and 13.6 per cent. reduction in area. A high cobalt content is noted in all these alloys. The comparable values for Konel metal aged at 650° C. and tested at 600° C. are proportional limit 15,000 lb., elongation 25 per cent. This compares with 23,000 lb. and 18.5 per cent. respectively for Konel quenched after a 23-hr. anneal at 900° C.

Perhaps the alloy presenting the most interesting mechanical properties after aging is the alloy designated 42B. With a proportional limit of 57,500 lb. at 600° C., this material exhibits an elongation of 21.5 per cent. and a reduction in area of 21.7 per cent. The high cobalt content (24.8 per cent.) is also accompanied by the introduction of chromium (18.7 per cent.). It is of interest to compare the properties of this alloy with those of the 70:30 nickel-chromium containing 0.4 per cent. carbon (alloy 9, Table 3). The substitution of cobalt for some of the nickel appears to produce an increase in ductility without loss of strength. More detailed experimental analysis of this group of alloys seems merited. This suggestion also applies to the evaluation of creep stresses for those alloys which show a good proportional limit at 600° C. along with the maintenance of some ductility.

A little closer correlation of the properties of these alloys with similar properties of a few well-known commercial alloys is possible by reference to Table 4. These alloys were aged and treated in a manner identical to those included in Table 2, hence the high-temperature test results have similar significance.

Several of the new alloys presented in this paper have at least twice the value, for proportional limit at 600° C., of those given in Table 4, but it must be observed that the ductility of the new alloys is not as satisfactory, although the amount of ductility desired may be considered

TABLE 4.—*High-temperature Tests on Some Commercial Alloys Performed in a Manner Identical to the Tests on Alloys in Table 2*

No.	Alloy Mark	Proportional Limit, Lb. per Sq. In.		Tensile Strength, Lb. per Sq. In.		Elongation, Per Cent. in 2 In.		Reduction in Area, Per Cent.		Remarks
		Normal Temp.	600° C.	Normal Temp.	600° C.	Normal Temp.	600° C.	Normal Temp.	600° C.	
1	K1965.....	20,000	19,000	128,000	80,600	30.5	20.7	40.5	42.5	Nonmagnetic alloy 18 per cent. Ti, 80:20 Ni Cr.
2	High speed.....	12,500	10,500	121,000	51,600	16.0	37.0	16.0	57.0	
3	Nichrome IV.....	27,500	18,000	117,500	83,000	35.0	15.5	48.0	17.5	
4	Resistal II <sup>a</sup> .....	27,500	24,000	117,750	75,000	47.5	33.5	55.5	50.0	
5	Resistal IV <sup>a</sup> .....	25,000	17,500	102,000	72,000	41.0	30.5	56.5	33.5	
6	Ascoloy 44 <sup>a</sup> .....	31,000	10,000	103,500	67,000	48.5	35.0	04.0	53.5	
7	Resistal 2600 <sup>a</sup> .....	42,000	25,000	99,500	65,000	41.5	14.5	57.0	22.2	

<sup>a</sup> See Amer. Soc. Test. Mat. (1930) Pt. 1 for chemical analyses of these commercial alloys.



## AGING CHARACTERISTICS

The aging characteristics are given as revealed by various time-temperature observations on the Vickers hardness of the alloys. In these aging experiments the method adopted to obtain the necessary data was to anneal the alloys for 1 hr. at 950° C. and follow by a water quench. The alloys were then aged at 600° C., 650° C., 700° C. or 750° C. and the Vickers hardness taken after increasing periods of time.

Much information has been accumulated on this phase of the work and it is considered that suitable presentation of a limited amount can be effected most briefly by discussing the problem under a few group headings depending on the nature of the results obtained, as follows:

*Rate of Age-hardening*

It was soon realized that some of the alloys aged rapidly, and in most cases about 80 per cent. of the maximum aging hardness was obtained

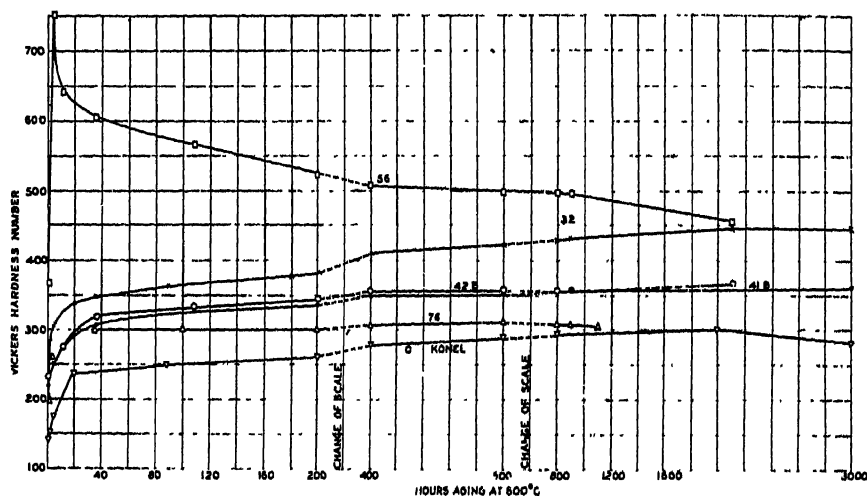


FIG. 3.—EFFECT ON VICKERS HARDNESS NUMBER OF AGING ALLOYS AT 600° C.

within about 72 hr. at 650° C. For this reason all aged tensile specimens were aged 72 hr. before test. The behavior of various alloys can be observed by a study of typical age-hardening curves for 600° C., 650° C. and 750° C. (Figs. 3-5). The hardness of alloy 32 rises from 220 as quenched, to 350 after 4 hr., and 400 after 20 hr. at 650° C. After 5 hr. the hardness of alloy 56 changed from 385 to 590, and then fell to 460, followed by moderate changes (Fig. 4). At 600° this alloy shows a hardness increase from 370 to 750 in 5 hr. and again falls away rapidly. In general, it has been stated that much of this aging takes place within the first few hours and that about 80 per cent. of the maximum increase has been effected after 72 hr. This refers to aging at 600° and at 650° C.

At 750° C. the aging is more rapid and the hardness soon begins to fall off again (Fig. 5).

### *Lack of Age-hardening*

While age-hardening is characteristic of most of the alloys examined, some striking cases were observed in the series, where little or no hardening followed the high-temperature anneal. A few of these alloys have been grouped in Fig. 6. The alloys exhibit practically no aging and

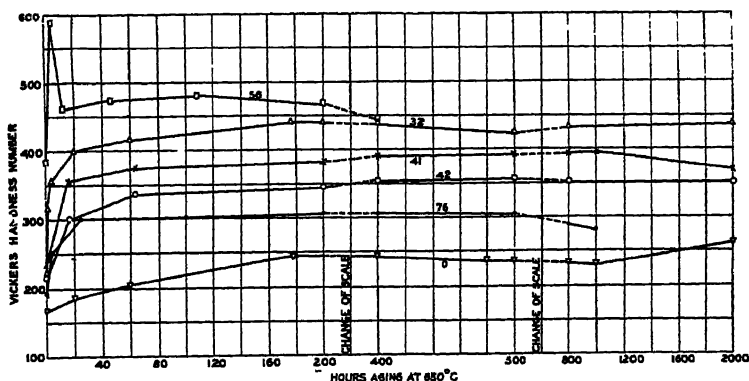


FIG. 4.—EFFECT ON VICKERS HARDNESS NUMBER OF AGING ALLOYS AT 650° C.

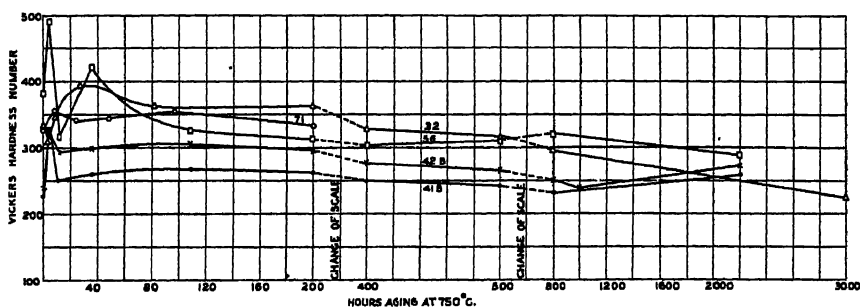


FIG. 5.—EFFECT ON VICKERS HARDNESS NUMBER OF AGING ALLOYS AT 750° C.

therefore apparently are similar in this respect to the pure iron-cobalt-nickel alloys. Pure titanium and ferrotitanium were both used in preparing alloy 29, which shows a little aging.

### *Factors Influencing Age-hardening*

The cause of age-hardening in these alloys has not been determined. It seems clear, as previously mentioned, that the simple ternary alloys are not subject to marked aging, and that the predominating factor is the titanium addition. Whether this is due to a separation of titanium or a titanium compound is not known. Some experiments were carried out to

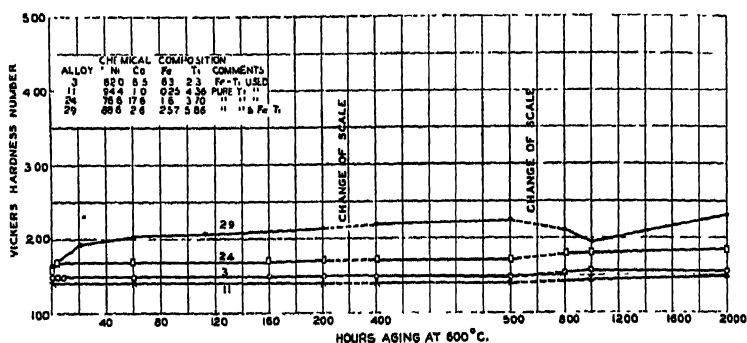


Fig. 6.—LACK OF AGE-HARDENING CHARACTERISTICS AT 600° C. IN CERTAIN TERNARY ALLOYS CONTAINING TITANIUM.  
Composition of alloys is given in Table 1.

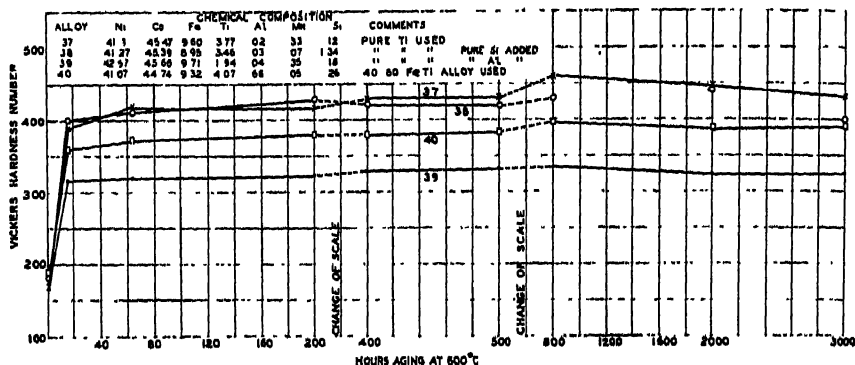


Fig. 7.—AGE-HARDENING CURVES INDICATING THAT PHENOMENON IS DUE TO PRESENCE OF TITANIUM AND NOT TO INCIDENTAL IMPURITIES.

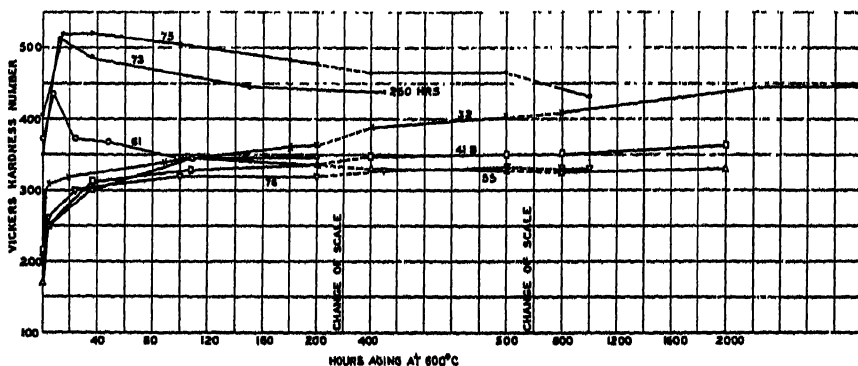


Fig. 8.—AGE-HARDENING CHARACTERISTICS AT 600° C. OF PARTICULAR ALLOYS USED IN BEND-TEST EXPERIMENTS.

examine the influence of the impurities contained in ferrotitanium on aging properties, and to determine whether such properties were different from those obtained when pure titanium and electrolytic iron were

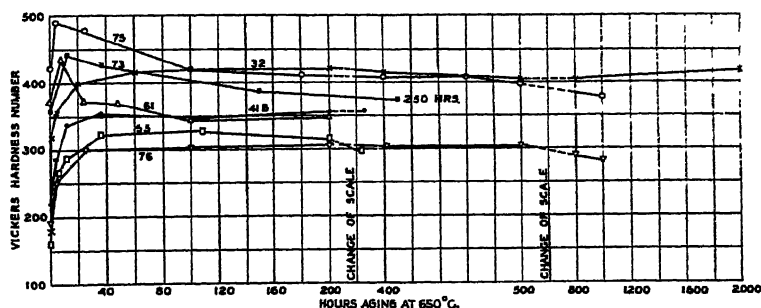


FIG. 9.—AGE-HARDENING CHARACTERISTICS AT 650° C. OF ALLOYS USED IN BEND-TEST EXPERIMENTS.

employed in the synthesis. The chemical analysis and aging features are presented in Fig. 7, along with details of making the alloys. This figure illustrates the evident role played by titanium in giving age-hardening characteristics to nickel-cobalt-iron alloys.

A general consideration of the data also suggests that aging is obtained only when appreciable quantities of both cobalt and iron are present in

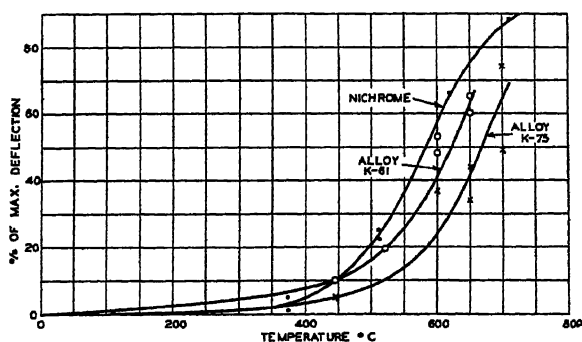


FIG. 10.—EFFECT OF TEMPERATURE ON BENDING OF METALS. NICHROME SERVES AS BASIS FOR COMPARISON.

the alloy. Thus alloy 24 (Fig. 6), which has high cobalt and titanium content, has but a small addition of iron, and exhibits practically no aging at 600° C.

#### *Aging Characteristics of Alloys Used in Bend Test*

In the next section the behavior of a few alloys in a new bend test is described. For the sake of completeness, the aging characteristics of this group of alloys at 600° C. and at 650° C. are illustrated in Figs. 8 and 9, respectively.

*Bend Test on Alloys*

No theoretical analysis of the bend test will be attempted. Attention will be directed only to the method of preparing test specimens, the nature of the bend test and the experimental results obtained.

In the preparation of the samples the 1-in. square hot-forged bar was thoroughly cleaned, further forged to  $\frac{3}{8}$  in. square and hot-rolled to about 0.150 in. square. The square wire was then cold-rolled to ribbon 0.017 in. thick and 0.125 in. wide. Intermediate annealing was necessary in some instances. The test strips finally were cut into  $5\frac{1}{2}$ -in. lengths. The strips were annealed in a flat form at 950° C. for 30 min. and rapidly

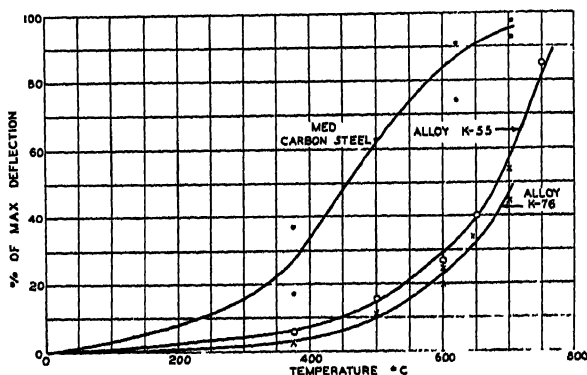


FIG. 11.—EFFECT OF TEMPERATURE ON BENDING OF METALS. MEDIUM CARBON STEEL SERVES AS BASIS OF COMPARISON.

cooled; then aged *in vacuo* at 650° C. for 72 hr., care being taken not to bend the specimens during handling. This produced flat strips ready for testing. The strips were next placed in a form of known radius and maintained 30 min. at the desired temperature.

The bend test consisted in preparing a flat strip, constraining it in a form of known radius for a definite time at the temperature of test, cooling, removing the strip from the form and measuring the amount of bend produced by a simple but extremely accurate method, as follows: The strip was laid across two pivots placed 4 in. apart. A fixed micrometer was then adjusted until contact was made at a point midway between the pivots. Errors due to contact pressure were avoided by using a grid glow tube.

Before the test, the strips were flat. The constraining device (called the "form") in which the strips were treated had a definite radius of curvature. After test, the strips always showed some radius of curvature less than that of the form. A measure of this curvature was obtained by noting the vertical displacement over the 4-in. length of specimen by use of the fixed micrometer, subsequent to the 30-min. constraining

period. The curvature of the form itself was fixed, of course, hence the vertical displacement in a 4-in. chord could be calculated readily. Then, Percentage of maximum deflection =

$$\frac{\text{Vertical displacement of strip after constraining}}{\text{Vertical displacement of form}} \times 100$$

In Table 5 are listed the temperatures required to produce 50 per cent. and 10 per cent. of maximum deflection in the various alloys. These temperatures were read off from the curves presented in Figs. 10, 11 and 12, where percentage of maximum deflection, as expressed by the above equation, is plotted against constraining temperature. The temperatures at which tests were carried out include 400°, 500°, 550°, 600° and 700° C. The results of these tests on nine materials are presented in Figs. 9, 10, and 11, and the composition of the alloys is given in Table 5. This compilation of the test results shows that the relative merits of the alloys, based on a percentage of maximum deflection of 50 per cent. and 10 per cent., merit the order in this table, the best alloy being placed at the head of the table.

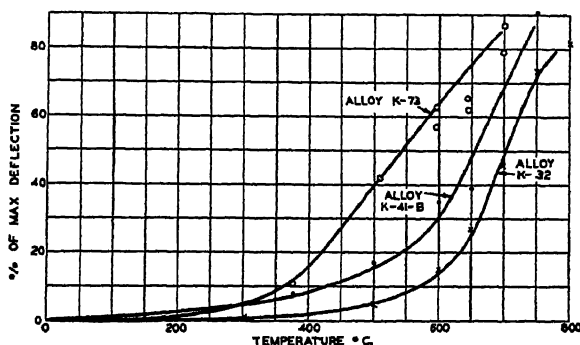


FIG. 12.—EFFECT OF TEMPERATURE ON BENDING OF METALS. ALLOY K32 IS MOST RESISTANT TO HIGH-TEMPERATURE DEFORMATION.

Table 5 shows also the chemical composition of the alloys considered in this section of the paper. Inspection of the various curves shows the great degree of variance among the different alloys. An alloy which has very little permanent set after heating at the test temperature is a desirable one, and the superiority of alloys 55 and 76, for example, over carbon steel is immediately evident.

Primarily this test provides a comparison of the various alloys with respect to their resistance to plastic deformation at elevated temperatures. This is a property which the usual tensile test does not reveal. Its importance is obvious in that an alloy to be employed for service at high temperatures should not be only of sufficiently high tensile strength but also should retain its initial dimensions under stress. The usual tensile

TABLE 5.—*Results of Experiments on Bend Tests Showing Various Temperatures Required to Maximum Deflection*

Alloy No.	Composition, Per Cent.						Temperature, Deg. C., Required for	
	Ni	Co	Fe	Ti	Cr	C	50 Per Cent Maximum Deflection	10 Per Cent Maximum Deflection
32	57	27	10	4.3		0.7	710	560
76	19.5	78		2.3			710	505
75		60	37.5	2.5			680	500
55	23	40	34	2.23		0.08	665	450
41B	49	29.5	8.4	2.4	9.5	0.02	660	445
61	5	19	72	2.5			600	435
"Nichrome" <sup>a</sup> ...						Mn		
	58.67		21.42		17.26	2.34	595	420
73	20	20	57.5	2.5			590	350
Medium carbon steel <sup>a</sup> .....						0.5	485	215

<sup>a</sup> "Nichrome" and medium carbon steel have been included in the test for purposes of comparison.

test shows the former but gives no index to the latter. The tensile test therefore is insufficient in selecting an alloy for a specific purpose.

It is of interest also to compare the percentage of maximum deflection in bending with the high-temperature physical tests. Such a comparison provides the data presented in Table 6. No data on proportional limit of the other alloys are available. Alloys 75 and 76 were said to be so hard that the threads broke on machining.

TABLE 6.—*Comparison between Proportional Limit and Maximum Bend Test Deflection at 600° C.*

Alloy No.	Proportional Limit at 600° C., Lb. per Sq. In.	Maximum Deflection at 600° C., Per Cent.
32	61,250	15.0
41B	52,500	32.0
55	36,250	29.0
61	12,500	50.0

Inspection of these limited data, however, suggests an inverse variation between proportional limit and percentage of maximum deflection. This further suggests a possible rapid method of analysis for high-temperature properties. Further work is necessary before comment can be made on the correlation that may be found to exist between these bend-test values and the so-called creep limit.

## GENERAL CONSIDERATIONS

It should be clearly understood that this paper is submitted as a progress report and, as such, outlines the development of the work on high-temperature alloys up to the present time. It constitutes an exploratory survey on the mechanical properties exhibited at 600° C. by alloys in the nickel-cobalt-iron ternary system containing additions of titanium, under fairly well defined conditions of test. Under similar test conditions a few commercial alloys have been examined, so that the test data are strictly comparable.

The highest proportional limit at 600° C. of these commercial alloys is about 25,000 lb. per sq. in. Among the new alloys proportional limits between 50,000 and 70,000 are recorded, although in some cases the ductility is low. One of the most promising alloys appears to be the one designated 42B, which at 600° C. has a proportional limit of 57,000 lb. per sq. in., 21 per cent. elongation and 21 per cent. reduction of area. A comparison of the tensile strength of this alloy with the 70:30 nickel-chromium alloy previously discussed (Table 3) again shows an apparent marked superiority for the new alloy. In 42B the ultimates at normal temperature and at 600° C. are 165,000 and 127,000 lb. respectively. In the 70:30 alloy at normal temperature and at 650° C. they are 153,000 and 105,000 lb. respectively. Analysis of the permissible creep stresses of this alloy, and other materials exhibiting similar values for proportional limit at high temperature is to be undertaken.

It would be of interest to compare some of the mechanical properties of these alloys with similar properties for iron-tungsten and iron-molybdenum alloys after age-hardening, but the only information available appears to be a measure of hardening at room temperature as the result of various high-temperature aging tests.

As regards the aging characteristics, the most interesting features are the initial rapid rate of aging of some of the alloys and the high temperature at which aging persists over prolonged periods. This surprisingly high temperature of aging argues well for the stability of the alloys at somewhat lower temperatures where the strength resulting from the age-hardening is of practical importance. Typical aging data which illustrate these points are reproduced in graphic form in the various diagrams.

As mentioned above, a limited comparison of these figures with those obtained by Sykes<sup>8</sup> on the iron-tungsten and iron-molybdenum alloys may be drawn. With 20 per cent. tungsten a 440-hr. aging at 600° C. appears to give a maximum hardness of about 330 Brinell. This hardening is comparable with some of the alloys used in the bend test (41B and 55). Alloys 32, 73 and 75 show considerably greater hardening proper-

<sup>8</sup> W. P. Sykes: The Iron-tungsten System. *Trans. A. I. M. E.* (1926) 73, 969.

The Iron-molybdenum System. *Trans. Amer. Soc. Steel Treat.* (1926) 10, 839.



ties. The most interesting feature of alloy 32 is the continuation of the age-hardening effect, which persists up to about 2000 hr. at 600° C. and then appears to maintain this maximum value (450 Vickers). Alloys 73 and 75 quickly reach hardness values above 500 Vickers and then slowly fall away to a value around 400. The most striking instance of rapid aging to a phenomenally high value is found in alloy 56, which in 4 hr. aging at 600° C. rises from about 360 to 750 Vickers hardness. At 650° C. a maximum of 590 is reached with equal rapidity. The iron-molybdenum alloys show more marked age-hardening than the iron-tungsten system but it is difficult to draw comparisons between the former series of alloys and the present alloys.

There seems little doubt that this aging is due to the presence of titanium in the alloys. In what form the separating constituent exists, however, is uncertain, although observations seem to indicate that both cobalt and iron must be present in quantity in order to produce the marked aging features developed at 600° C. The results of experiments illustrated in Fig. 5 suggest that the phenomenon is not due to the presence of impurities introduced with addition of commercial ferrotitanium. These alloys contain both aluminum and silicon in varying amounts.

Data on the new form of bend test are submitted in order to demonstrate how these high-temperature alloys behave under the given type of deformation at different temperatures. The actual temperatures considered lie at or below the temperature of preaging 650° C., with a few exceptions. Data on ordinary mild steel and 80:20 nickel-chromium alloy serve as a comparison basis for the results.

As previously indicated, it is believed that the test provides a useful comparison of the amount of plastic deformation of the alloys at high temperatures, and hence serves as a measure of the resistance to permanent deformation. The usual tensile test does not exhibit this property. It is hoped to analyze the possible correlation of this information with data on creep of some of the alloys when time permits.

#### ACKNOWLEDGMENTS

The authors are pleased to acknowledge the valuable assistance and cooperation obtained from several colleagues of the Westinghouse Electric and Manufacturing Co. in preparing the information for this paper, and to the executives for permission to publish the results. Messrs. McVetty and Crang are responsible for the mechanical test data and Mr. R. H. Wynne for the chemical analysis. Messrs. Newton and Shoup and Miss Ferguson have materially assisted in obtaining data on the aging properties and bend-test characteristics of the alloys. Finally, the authors desire to thank Mr. P. H. Brace for his constant encouragement throughout the course of the investigation.

## DISCUSSION

*(Norman B. Pilling presiding)*

N. B. PILLING, Bayonne, N. J. (written discussion).—It is possible to go somewhat farther than the authors have done in this interesting paper and point out that precipitation-hardening by means of titanium is not a special property of the nickel-cobalt-iron alloys which they have described, but appears to be characteristic of many types of alloy in which nickel likewise is present. A number of circumstances suggest that it is titanium in association with nickel that constitutes at least one form of the hardening precipitate; the suggestion given on page 96 that cobalt and iron appear to be essential may thus require some modification. In part, the types of base composition which are responsive to titanium include iron-nickel alloys, iron-nickel-chromium, nickel-chromium and nickel-copper, as well as many derivatives of these. The nickel-chromium-iron alloys constitute a group which is unquestionably of wider intrinsic engineering interest than expensive, high cobalt-content alloys, and the possibility of bringing about dependable improvements in elastic strength in austenitic nickel-chromium steels through the agency of precipitation-hardening is engaging attention. Of course, such high-strength alloys retain their superior strength characteristics only up to the precipitation-temperature range, which at the most is no higher than 1100° F. The fact that titanium becomes associated with nickel in the hardening precipitate assumes importance in attempts to improve such marginally austenitic alloys as 18 per cent chrome, 8 per cent nickel. The resultant withdrawal of nickel from solution throws such a composition into the martensitic field, and the hardness thus developed, often very high, does not persist to very high temperatures.

E. M. WISE, Bayonne, N. J.—I presume that the primary interest in the nickel-cobalt-iron titanium alloys arose in connection with their use in vacuum tubes, where oxidation is not a feature. It so happens that there seems to be a general association of high-temperature alloys with their ability to withstand heating in air to high temperature. I would, therefore, like to ask the authors what limitations in operating temperature are set by oxidation in air aside from those determined by loss of strength due to overaging.

J. W. JENKIN, Birmingham, England.—I am not quite sure what our Westinghouse friends have in mind, whether they are putting forward these alloys as casting materials or for forging purposes, but I hope they will not lose sight of the fact that in these days of complicated forgings it is essential that high-temperature alloys can be readily worked hot. I agree, of course, that these have been forged from 2-in. dia. cast bars down to 1-in., but we need something really forgeable.

Side by side with forgeability for high-temperature service is the need for oxidation resistance. High-temperature service presupposes subjection to the attack of gases. I should be glad to know whether our Westinghouse friends can give us any information as to the behavior of these materials under such conditions.

Toward the end of the paper, the authors seem to imply that the maximum deflection percentage, the figure they use as ordinate, is some sort of indication of creep. I hope that that may be so, but I might suggest perhaps that an alternative method, say by supporting strips of these materials, either as a cantilever or some other way and measuring deflection in bend form under given load, might be more directly an index of creep. I am, in fact, applying that method in my own laboratory in England and I have no doubt it has not escaped attention here.

G. P. HALLIWELL (written discussion).—This research started as a by-product from the development of the alloy which we named Konel, designated in the paper as K-0.

That alloy was developed with respect to its use in radio tubes. We found there that it had very distinct properties at the temperature of operation which were far better than those exhibited by platinum; that is, better emission, and better strength characteristics, while in vacuum at the temperature of operation.

There was a fair degree of resistance to oxidation, and the thought came to us that if this particular sample, which happened to be almost a slab in the dark, showed these properties, we ought to investigate the system for other alloys having better properties.

Some of the alloys have shown considerable resistance to oxidation at 600° C. While we have not made any quantitative tests, we have some qualitative data. For instance, I have in mind the alloys K-41 and K-42 in the paper, which have been aged at 600° C. for 4000 hr. That is a longer time than is indicated in the paper.

The samples were removed from the furnace after a definite period, prepared for the Vickers hardness test and then returned for additional aging; so that the periods of heating were cumulative. Each time that the sample was prepared for a hardness test the surfaces were polished so that good reflection could be obtained for the hardness reading. In the particular alloys I have mentioned, all that was necessary was to rub the alloy surface on a 3-0 emery paper. In other words, that film was very thin.

These two alloys have been used experimentally—I do not know the exact results obtained—as valves in gas engines at Westinghouse, and as plugs in die-casting machines where molten brass is cast into forms used in the industry. They stood up remarkably well, far better in the plugs in the brass than the steels that were recommended for the same purpose: so that from a qualitative standpoint, some of the alloys do show good resistance to oxidation. Chromium, of course, increases that resistance materially, and these alloys, K-41 and K-42, do show distinct resistance to oxidation.

With regard to the working properties of the alloys mentioned in the paper, until we developed the technique of casting and hot working they were all more or less difficult to forge. I must stress, however, that this is almost, one might say, a pure research rather than a practical work. Naturally we did not care to cast larger ingots than was necessary until we knew better how to handle them or whether they showed any promising leads. Some of the alloys of higher titanium content were very difficult to forge. On the other hand, Konel, when once its cast structure was broken down, could be drawn into the finest of wires with only occasional annealing.

While we did use small samples—8 kg. on most of the alloys—some of them were made in 250-lb. ingots and put through the regular shop practice; that is, they were put through a heavy forging operation, just as some of the larger steel shafts would be forged. In other words, they were put through the shop on a production schedule and they stood up very well.

I do not say that all the alloys of this system would forge easily, especially those of higher iron and titanium content, which are rather difficult to handle in this respect. Our intention was that these alloys would, of course, be for forging purposes rather than for castings.

Mr. Pilling speaks of the heat treatment of his nickel-chromium titanium steels.<sup>9</sup> Is that a heat treatment or an aging? Is it the same as heat-treating a steel?

N. B. PILLING.—You mean in terms of time?

G. P. HALLIWELL.—In terms of process.

N. B. PILLING.—It is aging.

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<sup>9</sup> See discussion of paper by F. E. Hensel: Age-hardening of Austenite. *Trans. A. I. M. E., Iron and Steel Div.* (1931) 280.

G. P. HALLIWELL.—I must say that those are very good figures, especially the proportional limits that are given. We thought we had some very good figures here.

I should like to direct Mr. Foley's<sup>10</sup> attention to Fig. 7. Apparently he and I have had the same thought and the same difficulties. We were trying to find out what caused all this aging. In Fig. 7 the four curves represent the alloys made from the pure substances. In one case aluminum and in another silicon were added, inasmuch as those two impurities were the main impurities in the ferrotitanium that was used.

In conversation, Mr. Comstock brought up the point that the paper mentions a 75-25 iron-titanium alloy which we used as a medium for introducing our titanium. This alloy did not conform strictly to this composition, since, because of its method of reduction, relatively pure titanium or ferrotitanium contains aluminum or silicon in varying amounts. This particular ferrotitanium contained about 6 per cent aluminum. A residual amount occurred also in the alloys.

It was with the idea of finding out the effect of this residual amount that we made these special alloys, and apparently these impurities do not have any effect on age-hardening, since all four alloys hardened relatively the same amount upon prolonged heating at the aging temperature.

With respect to the relationship between nickel content and aging, mentioned by Mr. Pilling and Mr. Foley, Fig. 6 shows the aging characteristics of alloys of high nickel but low cobalt content and low iron-titanium ratios. They have very little aging, so that it does not seem that in these particular alloys nickel is essential. There are the negative aging effects even although there is high nickel content.

N. B. PILLING.—If I might interject—the solubility for the hardening constituent at the high nickel end is perhaps greater.

G. P. HALLIWELL.—That may be. Using pure nickel we obtained no aging at all but great ductility.

The speaker from England, Dr. Jenkin, brought up the question of creep in connection with the bend tests. Mr. Scott, of the Westinghouse Research laboratories, when using this method of testing, has found that with some of his alloys he obtains a residual deflection when working at stresses below what we know as, or what we can determine as, the proportional limit. Thus it would appear that he is obtaining plastic deformation within a range that ordinarily may be considered elastic. Whether such values so obtained may be considered as an evaluation of the creep properties of an alloy I am not prepared to say at this time.

In connection with Mr. Pilling's discussion, I wish to say that during the long-time temperature aging of 4000 hr. or more the hardness of many of the alloys was practically constant after the first 100 to 125 hr. Apparently there was no increase or decrease on some of these alloys at this temperature, so that they would retain their high proportional limits and high hardnesses over an extended period of time in any installation operating at a moderately high temperature, such as an oil-cracking machine.

C. R. AUSTIN (written discussion).—I was pleased to have a few observations from my former colleague, Dr. Jenkin. The alloys on which we have presented test data may definitely be regarded as suitable for forging purposes. All high-temperature alloys present some fabrication difficulties, because it is this very factor, of course—resistance to ready deformation at elevated temperatures—that confers on the alloys the useful characteristic properties at elevated temperatures.

Mr. Halliwell's inclination to regard these alloys as difficult to forge depends more on his recollection of forging difficulties with alloys not included in the present paper.

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<sup>10</sup> Reference of footnote 9, 281.

With few exceptions, no alloys have been considered which did not show a 5 per cent elongation. Several alloys were prepared which gave practically no elongation in the 600° C. short-time tensile tests, and a few were so hard or brittle as to crack in heat-treating or fail in the threads while testing. These alloys, however, have not been included in the paper.

As far as forgeability in general is considered in connection with these particular alloys, much depends on the technique of preparation of the alloys. If the necessary care is taken in melting, in the method of introduction of the alloying elements, and in the casting, the alloys discussed in the paper are commercially forgeable.

Our work on high-temperature alloys is related to two quite distinct applications; one for thermionic purposes, the other for high-temperature engineering purposes.

Mr. Pilling mentions applications. This is a very important point, and many of us are familiar with instances where certain specific properties are most desirable at elevated temperatures. On the high-temperature engineering side, however, we have devoted our attention not to application so much as to the possibility of developing specific alloys showing high-temperature strength. In this case the criterion rests on a comparison of properties of these alloys with the properties of the best high-temperature alloys previously investigated. An effort to draw some comparison has been made in the paper. As regards Mr. Halliwell's reference to the use of these alloys as valves in gas engines, we do not have any specific information from the tests, but a favorable general report has been made on the manner in which the alloys stand up to this service test.

With reference to Dr. Jenkin's comment on the modification of the type of bend test, consideration has already been given to the idea of supporting these materials in cantilever or some other form, and of course there are pros and cons in any test. Whatever form of test is employed, it seems desirable to avoid concentration of stress so far as possible.

Mr. Wise has asked for data on limitations in temperature of operation of these alloys. We are not in a position to answer this question. In considering our present series of alloys, we have to bear in mind that there are two distinct phases of the problem of high-temperature strength. These refer to the strength of the solid solution per se and the strength due to precipitation-hardening. The present work deals essentially with the strength due to precipitation-hardening, but we have work on hand whereby we hope to reveal the nature of the solid solution strength at temperatures above those at which age-hardening can be effective. At the same time collection of data on resistance to oxidation will also be important.

There is one final point to which I will allude—the phenomenon of age-hardening in relation to the composition of the alloys. A study of the data suggests that to obtain marked age-hardening properties, both nickel and cobalt must be present along with some iron. For high-temperature strength, independent of aging, it seems that cobalt confers on nickel—and a very large number of the alloys we discuss are essentially nickel-base—a decided increase in the strength of the solid solution. These two factors are presumably cumulative.

Reference to the literature will show that between iron and titanium there is supposed to be formed the intermetallic compound  $\text{Fe}_3\text{Ti}$ . The tests on aged alloys presented in Table 2 of the paper were conducted on alloys containing about 2.5 per cent Ti, which requires a minimum of 7.5 to 8.0 per cent Fe to form the intermetallic compound. All the aged alloys discussed contained approximately this percentage or more of iron.

It would appear that the marked high-temperature strength of the alloys depends on a precipitation-hardening due to a separation of iron-titanium compound from the double nickel-cobalt solid solution.

# The Equilibrium Diagram of the Copper-rich Copper-silver Alloys

BY CYRIL STANLEY SMITH\* AND W. EARL LINDLIEF,\* WATERBURY, CONN.

(Boston Meeting, September, 1931)

A STUDY of the mechanical properties of the alloys of copper and silver led to the discovery that the solubility of silver in copper was greatly different from that generally supposed, therefore some work was done to determine the solubility with greater accuracy than had previously been achieved. After the work had been completed, two papers were published<sup>1</sup> giving solubility figures which agreed closely with one another and with the work described herein. A detailed comparison of that work with the present will be given later.

## PREPARATION OF ALLOYS

The copper used in making the alloys was electrolytic ingot of high purity. The silver was prepared by precipitation as chloride from nitric acid solution, followed by fusion of the washed precipitate with sodium carbonate and potassium nitrate. This method gives metal containing at least 99.99 per cent silver. The copper was first melted under charcoal in a small electric resistance furnace and the silver added as pure silver, it being unnecessary to make any intermediate alloys. After thorough stirring the metal was poured into a mold of suitable form. The alloys contained between 0.008 and 0.015 per cent of oxygen. Small amounts of oxide were visible under the microscope, but it is not believed this would have much effect on the results.

Copper-silver alloys are notorious for segregation, consequently a few experiments were carried out to find a form of casting with as little segregation as possible. A mold 6 in. long and  $\frac{1}{2}$ -in. dia. was first used, and an alloy nominally containing 5 per cent silver was cast in it, while some of the same alloy was poured directly into water to obtain the maximum rate of cooling possible. Analyses were made both on this sample and on turnings from the top and bottom of the  $\frac{1}{2}$ -in. dia. casting, the turnings being separated into three parts according to the position

\* Research Laboratory, American Brass Co.

<sup>1</sup> N. Ageew, M. Hansen and G. Sachs: *Entmischung und Eigenschaftänderung Übersättigter Silber-Kupferlegierungen. Ztsch. f. Phys.* (1930) **66**, 350.

D. Stockdale: *The Solid Solutions of the Copper-Silver System. Jnl. Inst. Metals* (1931) **45**, 127.

in the bar from which they had come. Fig. 1 shows a cross-section of the bar with the amount of silver found in the different parts indicated.

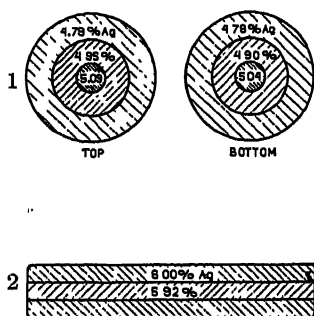


FIG. 1.—ANALYSES OF SECTIONS OF CASTING 6 IN. BY  $\frac{1}{2}$ -IN. DIA., SHOWING SEGREGATION. ALLOY CONTAINED 5 PER CENT SILVER.

FIG. 2.—ANALYSES OF SECTION OF CASTING 6 BY 1 BY  $\frac{3}{16}$  IN. ALLOY CONTAINED 5.98 PER CENT SILVER.

There is considerable axial segregation, although the two ends of the ingot differ but little.

To obtain more rapid cooling a mold was made of pure copper, which gave a casting 6 by 1 by  $\frac{3}{16}$  in., and since the mold weighed 18 times as much as the ingot, a very rapid chill was obtained. It was impossible to fill the mold unless it was warm and coated with dressing, but under these conditions good castings were obtained. Analyses of sections of castings made in this mold showed much less difference than before, although there was still some segregation, in this case inverse, as Fig. 2 shows. This method of casting was adopted as satisfactory, and a complete set of castings was made in this mold for the determination

of the solidus and solubility limit.

#### DETERMINATION OF LIQUIDUS

Although previous researches agree well as to the location of the liquidus, a few alloys were melted and cooling curves obtained using the methods of thermal analysis described in another paper by one of the authors.<sup>2</sup> The metal was covered with charcoal to prevent oxidation. The liquidus arrests observed are shown in the Table 1.

TABLE 1.—*Liquidus Arrests in Silver-copper Alloys*

Alloy No.	Silver, Per Cent	Temperature of Arrest, Deg. C.
323	2.103	1072
325	4.01	1061
327	5.97	1052
329	8.00	1043
331	9.96	1034
332	11.84	1024

#### DETERMINATION OF SOLIDUS

It was impossible, of course, to determine accurately the solidus from the cooling curves and even the eutectic temperature could not be deter-

<sup>2</sup> C. S. Smith: The Constitution of the Copper-silicon System. *Trans. A. I. M. E., Inst. Met. Div.* (1929) 414.

mined independently, since it was used as one of the fixed points for the calibration of the thermocouples. This temperature, however, has been determined recently with great accuracy by Roesser<sup>3</sup> at the U. S. Bureau of Standards, who found it to be  $779.4 \pm 0.1^\circ\text{C.}$  on the International scale.

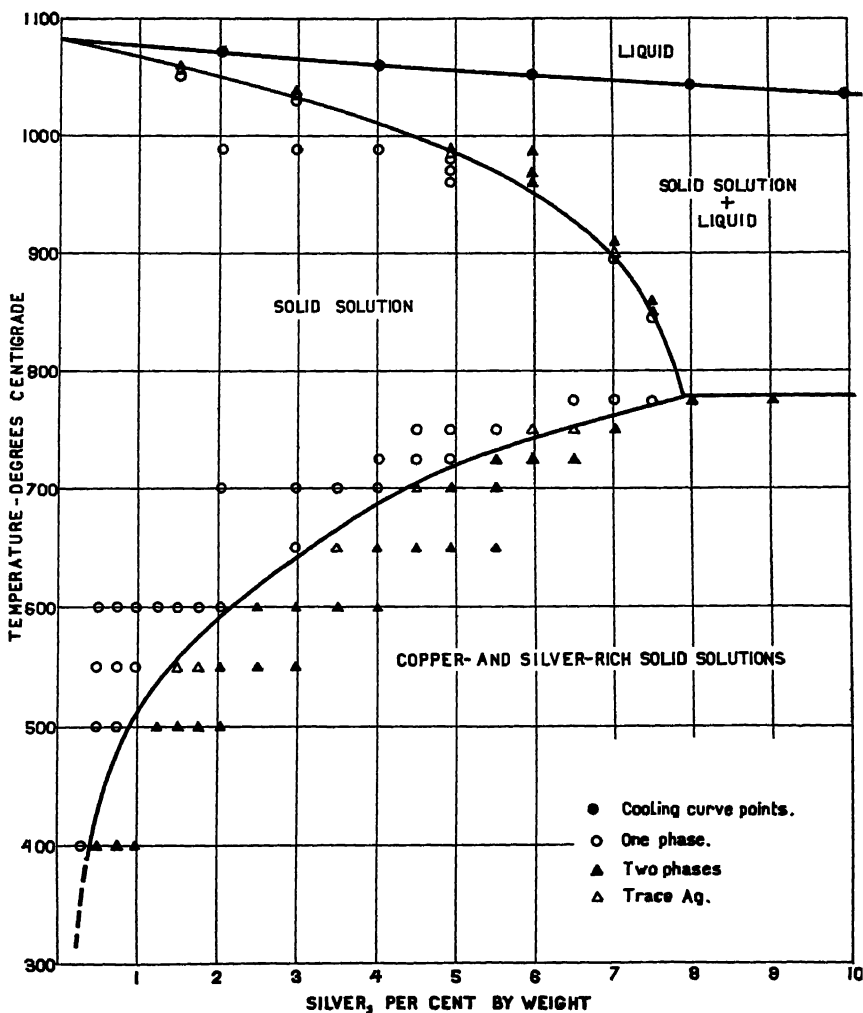


FIG. 3.—EQUILIBRIUM DIAGRAM OF COPPER-SILVER SYSTEM—0 TO 12 PER CENT SILVER.

The course of the solidus was determined by a series of annealing and quenching experiments. A number of castings made in the copper mold described above were first rendered as homogeneous as possible by

<sup>3</sup> W. F. Roesser: Thermo-Electric Temperature Scales. U. S. Bur. Stds. *Jnl. of Research* (1929) 3, 343.



annealing for 24 hr. at 700° C., and afterwards were quenched and cold-rolled to 0.15 in. thick (20 per cent reduction of area) prior to being cut up into microsamples of suitable size. Samples of suitable composition were rapidly heated to the eutectic temperature and annealed there for 1 hr., after which the temperature was raised to the desired value in the neighborhood of the solidus and held there for 30 min. prior to quenching the sample in water. This annealing time was sufficient to show the equilibrium structures, since an alloy cannot be heated beyond the solidus even for a short time without liquid appearing. Examination of the microstructures after polishing and etching showed readily whether the solidus had been passed or not. Fig. 4 is a photomicrograph of a typical sample containing an excess of liquid at the moment of quenching. The annealing was repeated at a higher or lower temperature until the solidus had been suitably bracketed. Table 2 lists the structures observed. The points are also incorporated in the diagram, Fig. 3, which shows all the experimental results and the curves obtained.

TABLE 2.—*Structure of Alloys Annealed for Solidus Determination*

Alloy No.	Silver, Per Cent	Temperature of Anneal, Deg. C.		
		[No Liquid	Trace Liquid	Much Liquid
343	1.50 <sup>a</sup>	1050	1055	1060
324	2.97	1030, 1035		1040
326	4.93	970, 980	985	990
327	5.97		960	970, 988
328	7.01	895	900	905
350	7.50 <sup>a</sup>	845	850	860

<sup>a</sup> These alloys not analyzed. Synthetic composition given.

### SOLID SOLUBILITY

The solubility below the eutectic temperature was determined by examining samples after long annealing at various temperatures. The annealing was performed on sections of the cold-worked previously homogenized alloys, in a resistance tube furnace packed with charcoal to maintain a nonoxidizing atmosphere. The temperature was controlled to within  $\pm 2^\circ$  C. and is believed to have been within  $5^\circ$  of the absolute temperature desired. The samples were held in a heavy copper container, which was removed and the samples thrown out into water at the termination of the anneal. The quenched samples were examined under the microscope to determine the presence or absence of undissolved silver, the data being given in Table 3 and in Fig. 3. The curve drawn through the points in Fig. 3 shows that the maximum solubility of silver in copper is 7.9 per cent at the eutectic temperature, decreasing to

TABLE 3.—*Microstructure of Alloys Annealed for Solubility Determination*

Alloy No.	.....	361	340	341	322	342	343	344	323	345	324	346	325	347	326	348	327	340	328	350	329	330
Silver, per cent.	.....	0.299	0.501	0.75 <sup>a</sup>	0.98	1.25 <sup>a</sup>	1.50 <sup>a</sup>	1.75 <sup>a</sup>	2.03	2.50 <sup>a</sup>	2.97	3.50 <sup>a</sup>	4.01	4.50 <sup>a</sup>	4.93	5.50 <sup>a</sup>	5.97	6.50 <sup>a</sup>	7.01	7.50 <sup>a</sup>	8.00	9.03
Temp., Deg C.																						
Time, Hr.																						
400																						
500	o	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
550		o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
600		o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
650		o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o	o
700																						
725																						
750																						
775																						

o—Homogeneous X—Two phases, x—Trace silver.

<sup>a</sup> These alloys were not analyzed. Synthetic composition given

between 0.3 and 0.5 per cent at 400° C. The solidus, falling slowly to 4 per cent silver, drops very rapidly beyond 7 per cent to meet the eutectic horizontal at 7.9 per cent silver.

### MICROSTRUCTURE

Considerable difficulty was encountered in obtaining a satisfactory etching reagent to develop the structure of the alloys clearly. The excess silver in the alloys that had been quenched from a high temperature existed in comparatively large rounded particles and could be made to stand out clearly by etching with copper-ammonium chloride, ammonium persulfate or cathodic etching.<sup>4</sup> Ammonium persulfate was preferred, however, since it gave a very clean etch. If the film deposited on the surface was permitted to remain in place, the degree of contrast was amazing, for the silver remained perfectly white and shone out unmistakably under the microscope. Figs. 5 and 6 illustrate this well, while Fig. 7 shows a sample with no free silver etched to show grain contrast.

The samples which had been annealed at 600° C. and below contained silver in the form of finely divided particles and patches of a pearlitic nature and a very careful etching was necessary to develop the structure. Copper-ammonium chloride gave a thin dark film and permitted the tiny particles of silver to be distinguished, while the persulfate film masked them completely. For the development of the localized patches containing considerable amounts of finely precipitated silver, the best etch was found to be a solution containing 15 per cent ammonium persulfate and 6 per cent ammonium hydroxide (0.90 sp. gr.). This acts quite differently from ammonium persulfate alone, since it produces no film on the copper and etches the silver black. A tendency to form etch pits prevents its use on the high-temperature samples, although pits can easily be distinguished from the silver in samples annealed at the lower temperatures on account of the characteristic form of the latter. For the detection of the last traces of silver, the ammonium persulfate and ammonia etch was not satisfactory, and in this case copper-ammonium chloride gave the best results. It was only after repeated repolishing and re-etching and observation by two observers that the presence or absence of the last traces of silver in the samples annealed at the lowest temperatures could be determined

<sup>4</sup> C. S. Smith: Note on Cathodic Disintegration as a Method of Etching Specimens for Metallography. *Jnl. Inst. Metals* (1927) 38, 133.

FIG. 4.—ALLOY 324, 2.97 PER CENT SILVER. QUENCHED FROM 1040° C. × 200.

FIG. 5.—ALLOY 328, 7.01 PER CENT SILVER. ANNEALED 24 HR. AT 750° C. × 200.

FIG. 6.—SAME AS FIG. 5. × 500.

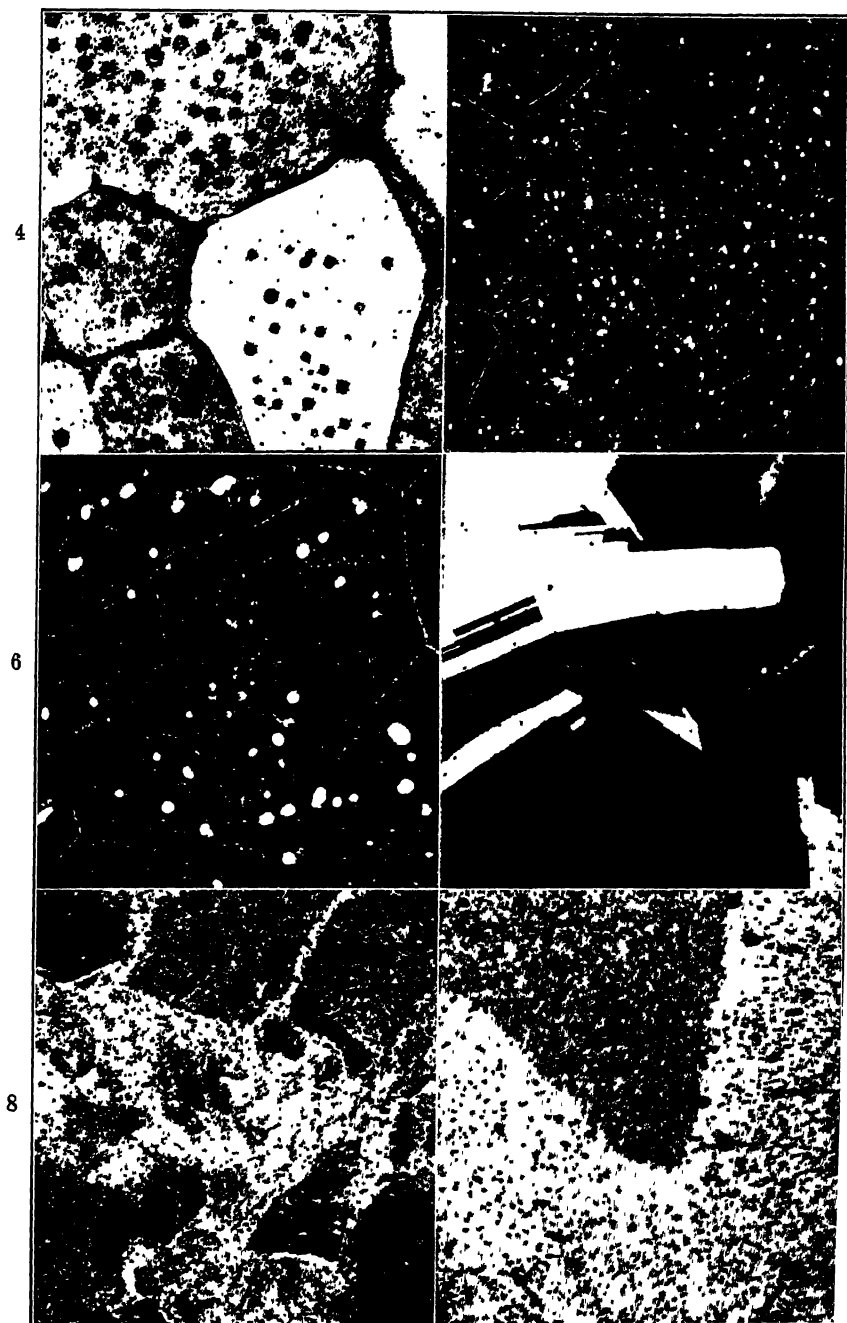
FIG. 7.—ALLOY 324, 2.97 PER CENT SILVER. ANNEALED 36 HR. AT 700° C. × 200.

Figs. 3-7 etched with ammonium persulfate.

FIG. 8.—ALLOY 324, 2.97 PER CENT SILVER. ANNEALED 96 HR. AT 550° C. × 200.

Etched with ammonium persulfate and ammonia.

FIG. 9.—SAME AS FIG. 8. × 500.



FIGS. 4-9.—CAPTIONS ON OPPOSITE PAGE.

definitely, but agreement was reached eventually and there is no doubt about the microstructures as finally decided upon and listed in Table 3.

At temperatures between 500° and 600° C. precipitation of silver on reannealing takes place generally throughout the grains (Figs. 8 and 9). The mechanism of precipitation of silver at low temperatures is interest-

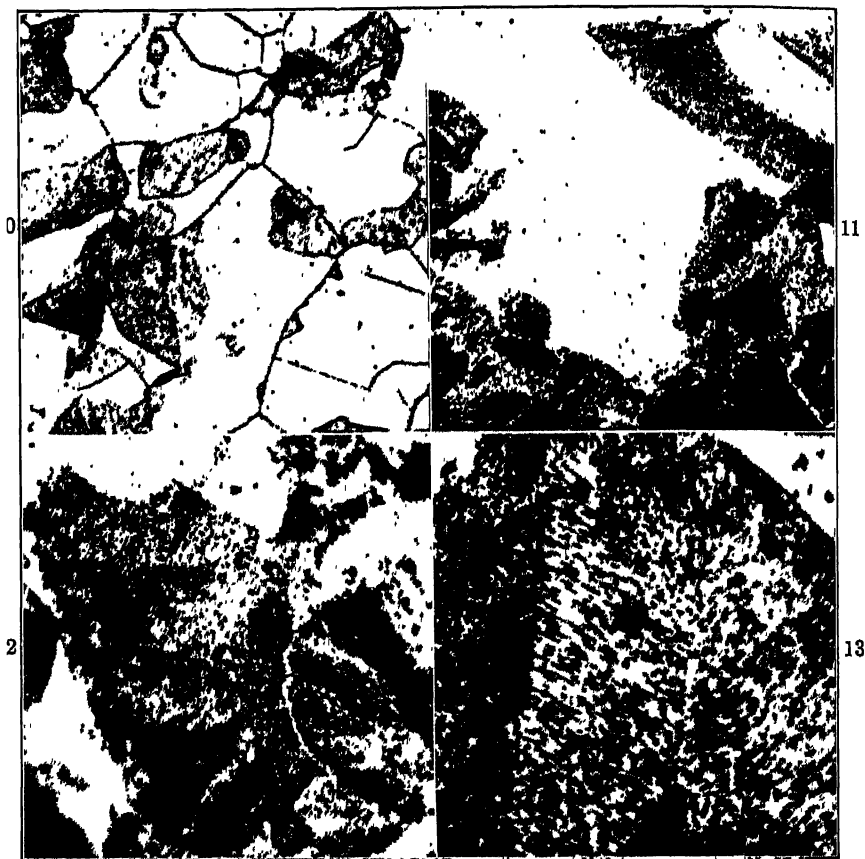


FIG. 10.—ALLOY 335, 3.94 PER CENT SILVER. ANNEALED 4 HR. AT 400° C.  $\times 500$ .

FIG. 11.—ALLOY 324, 2.97 PER CENT SILVER. ANNEALED 408 HR. AT 400° C.  $\times 200$ .

FIG. 12.—SAME AS FIG. 11.  $\times 500$ .

FIG. 13.—SAME AS FIG. 11.  $\times 1000$ .

All etched with ammonium persulfate and ammonia.

ing. It forms in patches starting from the grain boundaries and growing into the grains. After a long anneal the areas are completely decomposed and can be resolved at a magnification of 500. Fig. 10 shows the areas forming after a 4-hr. anneal, and Fig. 11 after 408 hr. at 400° C. Figs. 12 and 13 show this at higher magnifications. Whether or not the unprecipitated areas contained silver in metastable solution is not

known. The X-ray work of Ageew, Hansen and Sachs<sup>5</sup> and Sachs<sup>6</sup> has shown that the appearance of the stable lattice on reannealing a quenched alloy is sudden, and the new lattice coexists with the original lattice, there being no intermediate state. This indicates that the pearlitic patches represent complete decomposition into the equilibrium state, while the undecomposed areas represent the unchanged original composition. This would indicate a remarkable stability of the residual metastable alloys, for the relative area of the patches does not change much with increasing time, which has the effect only of coarsening the particles.

The structure of these precipitated grains was somewhat reminiscent of pearlite, although more often it consisted of small dots or slightly elongated particles and a well defined plate structure was rarely seen. An apparent Widmanstätten structure occasionally appeared but this was probably due to precipitation occurring along slip planes due to cold work.

#### REVIEW OF LITERATURE AND COMPARISON WITH PRESENT WORK

The silver-copper system was one of the very earliest to be subjected to scientific examination. Levol<sup>7</sup> knew of the constant temperature of solidification of the eutectic and, since there was no segregation, supposed it to be a compound. Roberts-Austen,<sup>8</sup> using the calorimeter method, determined the liquidus in 1875, and in 1897 Heycock and Neville<sup>9</sup> determined the diagram, using a resistance pyrometer, and obtained remarkable accuracy. Friedrich and Leroux<sup>10</sup> redetermined the liquidus and made slight changes, their diagram showing the eutectic at 778° C. and 72 per cent silver, instead of 779° C. and 71.9 per cent silver given by Heycock and Neville. Their liquidus and solidus were accepted until very recently, when the eutectic temperature and composition were redetermined by Roesser<sup>11</sup> and Stockdale<sup>12</sup> respectively. Roesser gave the value  $779.4 \pm 0.1^\circ$  C. for the temperature while Stockdale gave 71.94 per cent silver as the eutectic composition. Both of

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<sup>5</sup> N. Ageew, M. Hansen and G. Sachs: Entmischung und Eigenschaftänderung Übersättiger Silber-Kupferlegierungen. *Ztsch. f. Phys.* (1930) **66**, 350.

<sup>6</sup> G. Sachs: Suppressed Constitutional Changes in Alloys. *Trans. A. I. M. E. Inst. Met. Div.* (1931) 39.

<sup>7</sup> A. Levol: Memoire sur les Alliages, Considérés sous le Rapport de leur Composition chimique. *Ann. Chim. Phys.* (1852) **36**, 193.

<sup>8</sup> W. C. Roberts (-Austen): On the Liquation Fusibility and Density of Certain Alloys of Copper and Silver. *Proc. Roy. Soc.* (1875) **23**, 481.

<sup>9</sup> C. T. Heycock and F. H. Neville: Complete Freezing-Point Curves of Binary Alloys Containing Silver or Copper together with Another Metal. *Phil. Trans. Roy. Soc.* (1897) **A189**, 25.

<sup>10</sup> K. Friedrich and A. Leroux: Kupfer, Silber und Blei. *Metallurgie* (1907) **4**, 293.

<sup>11</sup> W. F. Roesser: *Loc. cit.*

<sup>12</sup> D. Stockdale: The Composition of Eutectics. *Jnl. Inst. Metals* (1930) **43**, 193.

these seem to have been determined with considerable care and undoubtedly are accurate. The portions of the liquidus curves up to 10 per cent silver determined by Heycock and Neville, Friedrich and Leroux, Hirose<sup>13</sup> and the present authors are all so close that they can scarcely be distinguished. This is to be expected, since thermal analysis is so simple and accurate a method for the determination of liquidus lines.

There has been less agreement between the various determinations of the solid solubility of silver in copper. Mattheissen<sup>14</sup> carried out electrical conductivity determinations which indicated 10 per cent as the solubility. Osmond<sup>15</sup> as a result of microscopic examination of very slowly cooled alloys concluded that the solubility was about 1 per cent at each end of the diagram. Kurnakow, Pusehin and Senkowsky<sup>16</sup> from conductivity and hardness measurements concluded that the solubility was about 6.6 per cent, while Lepkowski<sup>17</sup> by annealing at 750° C. found a limit of about 7 per cent. Erdal<sup>18</sup> and Weinbaum<sup>19</sup> both determined the solubility limits by determinations of crystal structure, placing the limits at 10.6 and 3.0 per cent silver respectively.

All the observers mentioned seem to have been unaware of the change of solubility with temperature and mostly have confined their measurements to one temperature only. Johansson and Linde<sup>20</sup> from their electrical conductivity measurements were the first to detect the difference in solubility. They obtained values of 8.2 and 1.68 per cent silver at 750° and 350° C. respectively. Their results are shown in Fig. 14, together with all the more recent determinations for comparison. Hirose<sup>21</sup> determined the complete diagram and supposed the solubility of silver in copper to be 5.3 per cent at the eutectic temperature and nil at 600° C. and below. Moller<sup>22</sup> determined the electrical conductivity of three

<sup>13</sup> T. Hirose: On the Silver-Copper Alloys. Rept. Imp. Mint. Osaka (1927) 1, 1.

<sup>14</sup> A. Mattheissen and C. Vogt: On the Influence of Temperature on the Electric Conducting Power of Alloys. *Phil. Trans. Roy. Soc.* (1865) A154, 167.

<sup>15</sup> F. Osmond: Sur les Alliages du Groupe Argent-Cuivre. *Compt. rend.* (1897) 124, 1234.

<sup>16</sup> N. Kurnakow, N. Pusehin and N. Senkowsky: Die Elektrische Leitfähigkeit und Härte der Silber-Kupferlegierungen. *Ztsch. f. anorg. Chem.* (1910) 68, 123.

<sup>17</sup> W. v. Lepkowski: Über den Einfluss der Abkühlungsgeschwindigkeit auf Zusammensetzung gesättigter Mischkristalle. *Ztsch. f. anorg. Chem.* (1908) 59, 285.

<sup>18</sup> A. Erdal: Contribution to the Analysis of Mixed Crystals and Alloys. *Ashandl. Norske Videnskapakademi Oslo* (1925) i, No. 12.

<sup>19</sup> O. Weinbaum: Über die röntgenographische Bestimmung der Mischkristallbildung von Silber-Kupferlegierungen. *Ztsch. f. Metallkunde* (1929) 21, 397.

<sup>20</sup> C. H. Johansson and J. O. Linde: Elektrische Leitfähigkeit und Zustandsschaubild der Kupfer-Silberlegierungen. *Ztsch. f. Metallkunde* (1928) 20, 443.

<sup>21</sup> Hirose: *Loc. cit.*

<sup>22</sup> F. Moller: Über die Löslichkeit von Silber in Kupfer. *Metallwirtschaft* (1930) 9, 879.

alloys from room temperatures to the liquidus and gave the results shown in Fig. 14. His maximum solubility was 7.0 per cent silver, a value which decreased to 3.9 per cent at 529° C.

Working independently and by different methods, Ageew, Hansen and Sachs<sup>23</sup> and Stockdale<sup>24</sup> obtained almost identical results, and the agreement of these two with each other and with the present work, per-

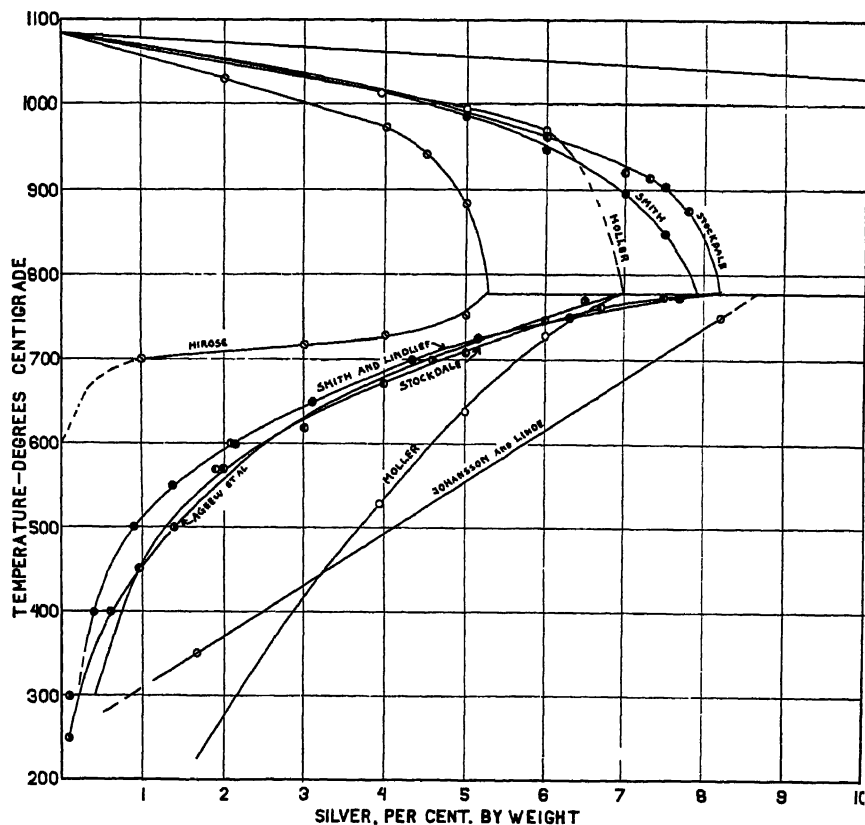


FIG. 14.—COMPARISON OF SMITH AND LINDLIEF EQUILIBRIUM DIAGRAM OF COPPER-SILVER SYSTEM WITH RESULTS OF EARLIER OBSERVERS.

formed before either was published, is very gratifying. Fig. 14 includes their results also. Ageew and his collaborators determined the curve up to the eutectic temperature by X-ray means, comparing the parameter of an alloy with 10 per cent silver which had been annealed and quenched

<sup>23</sup> N. Ageew, M. Hansen and G. Sachs: *Loc. cit.*

<sup>24</sup> D. Stockdale: The Solid Solutions of the Copper-Silver System. *Jnl. Inst. Metals* (1931) 45, 127.



from various temperatures with the curve obtained from a series of alloys of various silver contents quenched from the homogeneous range. Stockdale used both micrographic and electrical resistance methods with good agreement. His samples for microscopic examination were annealed for from 2 hr. to 3 days after a preliminary homogenizing anneal at 820°. Three days would probably not be sufficient time to enable equilibrium to be reached at the lower temperatures and the smaller solubility found by the present work is undoubtedly due to the fact that a closer approach to equilibrium was obtained. At 400° C. the annealing time used by the present authors was 17 days and at 725°, 24 hr. At high temperatures the difference is much less, probably because Stockdale's alloys were completely homogenized before treatment and 2 hr. of further annealing was sufficient. One of Stockdale's points (2.89 per cent at 645° C.) determined by electrical conductivity measurements on an alloy annealed until no further change occurred fits more closely on the authors' curve than on that of Stockdale, a fact which indicates that the latter's curve does not represent complete equilibrium at the lower temperatures. Stockdale took exceptional care to homogenize his alloys and it is probable that his solidus curve is more correct than that of the authors.

In spite of the greater sensitivity of the X-ray method it is probable that Ageew's alloys were also not sufficiently annealed. The diversion between his results at high temperatures and those of both Stockdale and the present work is due to the fact that the curve is so flat that extrapolation is difficult. Moreover, it is quite likely that an alloy as unstable as those high in silver when quenched from a high temperature would decompose slightly during quenching or before the exposure could be made. This would naturally indicate a lower solubility than the real one.

Drier<sup>25</sup> detected lines due to undissolved silver in X-ray diffraction patterns of copper containing as little as 0.003 per cent silver, and concluded that the solubility of silver in copper at room temperatures was less than this amount. Even quenched alloys showed the lines.

#### MECHANICAL AND ELECTRICAL PROPERTIES

A series of tests was made to determine the mechanical and electrical properties of the copper-silver alloys, and since these are of interest in relation to the diagram, curves for a typical alloy are given in Fig. 15. This shows the tensile strength, elongation and electrical conductivity of an alloy containing 4.98 per cent silver, 0.004 per cent iron, 0.011 per cent oxygen and 0.003 per cent sulfur. The metal was in the form of wire 0.080-in. dia. which was annealed for 4 hr. at 750° C.

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<sup>25</sup> R. W. Drier: An X-ray Study of the Copper End of the Copper-Silver System. *Ind. & Eng. Chem.* (1931) 23, 404; discussion, 969.

and quenched prior to reannealing treatment for 4 hr. at the temperatures shown in the figure. It is obvious from the curves that, while the electrical conductivity can be greatly increased by reannealing at a suitable temperature to cause precipitation of silver, this can only be achieved at the expense of both tensile strength and ductility. On the other hand, the Rockwell hardness of alloys containing more than 2 per cent silver does increase on suitable treatment. The hardness of the alloy containing 5 per cent silver was increased from 68 to 78 Rockwell (B  $\frac{1}{16}$ , 60 kg.) by annealing for 4 hr. at 400° C. after a 750° C. quench. Ageew, Hansen and Sachs found greater increases in hardness in alloys richer in silver, their alloy containing 10.5 per cent silver increasing from 71 to 96 Brinell after annealing at 400° C. Even this hardening is not nearly as great as that which occurs at the silver end of the system and which is accompanied by a simultaneous increase in tensile strength. It is interesting to note that maximum hardness of the copper-rich alloys occurs at a point where the tensile strength has decreased considerably below that of the quenched alloy. This is a most unusual effect, although many cases are known in which a considerable increase of hardness is accompanied by only a slight increase in tensile strength.

The relatively small amount of hardening due to precipitation might possibly have been due to the fact that the quenched alloys were already in a precipitation-hardened condition owing to partial decomposition on cooling, but that this was not the case was shown both by the low electrical conductivity of the quenched alloys and by the fact that quenching at different speeds had no effect on the hardness unless the cooling rate was of the order of one minute or more, while the samples considered had been quenched very rapidly in cold water. Furthermore, the X-ray examination of Ageew, Hansen and Sachs<sup>26</sup> has shown that quenching undoubtedly retains the silver in solid solution. It is obvious, therefore, that the alloys do not harden by precipitation of the silver as much as one would expect and the fully precipitated alloys are actually lower in tensile strength than the alloys in the quenched condition. Although

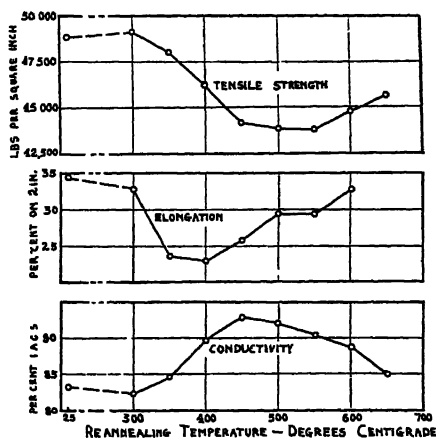


FIG. 15.—EFFECT OF REANNEALING ON PROPERTIES OF A COPPER-SILVER ALLOY (4.98 PER CENT SILVER) QUENCHED FROM 750° C.

<sup>26</sup> N. Ageew, M. Hansen and G. Sachs: *Loc. cit.*

there is yet no proof, this is possibly due, as Mohl<sup>27</sup> suggests, to the fact that "the silver solid solution precipitates with its plane of easy slip parallel to the plane of easy slip in the copper solid solution matrix." This would prevent the keying action of the precipitate and since the silver would be removed from the solid solution it would not produce the usual solution hardness.

### SUMMARY

The equilibrium diagram of the copper-silver system from 0 to 12 per cent silver has been redetermined. The liquidus agrees well with previous investigations, while the solid solubility determined by the microscopic examination of quenched samples was found to be 7.9 per cent at the eutectic temperature, 779.4° C. The solubility decreases rapidly below this point, becoming 4.4 per cent at 700°, 2.1 per cent at 600°, 0.90 per cent at 500° and about 0.4 per cent at 400° C. and below. This solubility curve is in good agreement with those recently published by Stockdale and by Agnew, Hansen and Sachs. The age-hardening which would be expected to result from this change in solubility was not realized, and there was actually a decrease in tensile strength caused by precipitation, although high electrical conductivities were obtained in alloys annealed at low temperatures.

### ACKNOWLEDGMENTS

The authors wish to express their thanks to Mr. W. H. Bassett for his real interest and encouragement during the work described and for his permission to publish the results. They also wish to acknowledge the help of those members of the staff of the Chemical Laboratory of the American Brass Co. who made special analyses on the alloys.

### DISCUSSION

*(John L. Christie presiding)*

R. F. MEHL, Middletown, Ohio (written discussion).—The demonstration by Agnew, Hansen and Sachs that precipitation in the silver-copper system does not take place gradually, with a solid solution matrix continuously impoverished in silver (or copper), and therefore with a gradually changing lattice parameter, but suddenly, marks this system as unique among those studied from this point of view. Sachs has demonstrated elsewhere that aluminum-copper alloys with 0 to 5 per cent Cu show on precipitation a gradually changing lattice parameter of the aluminum-rich solid solution, by which the extent of precipitation may be measured. Messrs. Smith and Lindlie now present photomicrographic evidence that precipitation here is not uniform and gradual over the piece, but sudden in patches, which gives a reasonable picture—however difficult to understand—of the course of this sudden alteration in lattice parameter.

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<sup>27</sup> R. F. Mohl: Private communication to the author, January, 1931.

Whether these unexpected and interesting facts may be determined by the type of crystallographic mechanism operating during the precipitation, and whether this type of crystallographic mechanism—the Widmanstätten mechanism—may account for the low aging capacity of the alloys, cannot as yet be said. Certainly the type of Widmanstätten mechanism in this system must be very unusual, for both participating phases are face-centered cubic but differ in the length of the side of the unit cube by approximately 10 per cent. In such a system, no two atom planes—one in each phase—can be selected which are more nearly similar geometrically and dimensionally than any other two planes, nor are the dimensions on any of these planes very nearly alike; they differ by 10 per cent. In such a case, the precipitate lattice may form from the solid solution lattice bodily, one unit cube of the matrix transforming directly without reorientation to one unit cube of the precipitate. If this were true, the planes of early slip in the two phases would be parallel, and the age-hardening capacity largely prevented. This was the sense of the “private communication” early this year.

Such a suggestion is, however, nothing but a random guess. Efforts to prepare typical Widmanstätten figures in these alloys produced only those “pearlitic structures” observed by the authors. Occasionally well defined plates were obtained, but no information has as yet been derived from their study. It seems clear that a direct determination of the orientation of the lattice of the precipitate in its relationship to the orientation of the lattice of the parent solid solution is the only possible method of attack. So far no success has attended such efforts.

The choice of the term “pearlitic” to describe the structures is a happy one, better than “eutectic,” which has frequently been used in similar instances. The term “eutectic” should be applied with discretion; a “eutectic” structure is not one of characteristic appearance—this varies extremely from system to system—but one formed during a specialized freezing process. Indeed, the general excellence of this work requires comment. Possibly no better could be made than to remark that it is of the same degree of excellence as the previous contributions of Dr. Smith on the study of the constitution of alloy systems.

D. STOCKDALE, Cambridge, England (written discussion).—It is most gratifying to me that the authors’ results are in such close agreement with mine and that the two sets are also in agreement with the X-ray evidence.

I differ from the authors in that I show a slightly greater solubility of silver in copper (approximately 0.3 per cent) at all temperatures. An attempt to explain this slight discrepancy may be of interest. First, I cannot accept the criticism that three days are insufficient to bring the alloys into equilibrium. My electrical conductivity experiments have shown that 12 hr. at temperatures as low as 450° C. are amply sufficient for this purpose. I believe that the alloys I examined were in absolute equilibrium. That being so, two possible causes of the difference suggest themselves to me:

1. The authors may have used the etching reagent in a more skilful manner and therefore have been able to detect traces of silver which I have missed. Their work will therefore be more correct than mine.

2. The authors may have used less pure materials. My copper was melted under hydrogen and therefore probably contained only traces of oxygen. It contained less than 0.0035 per cent of other impurities. It is to be expected that any impurity will hasten the appearance of the silver-rich and liquid phases, and that this effect will be most marked at those temperatures where the solubility of silver is small and at the solidus just over the temperature of the eutectic. It is at those temperatures that the two diagrams differ most widely, and it is to be remarked that at the lower temperatures Ageew, Hansen and Sachs are in closer agreement with me than with the authors.

The authors say, "One of Stockdale's points determined by electrical conductivity measurements . . . fits more closely in the authors' curve than on that of Stockdale." This statement is true, but it seems to me that this point is also definitely off their curve and that it is a mistake to use it as evidence.

These are minor criticisms and I hope that they will in no way disguise the very close agreement between Dr. Smith and Mr. Lindlieff and myself.

N. W. AGGEW, Leningrad, U. S. S. R. (written discussion) --The decomposition of supersaturated solid solution, which changes the concentration with the temperature, can proceed by two different processes.

In the first process the decomposition of a solid solution by tempering of the quenched alloy takes place by the gradual changing of its concentration. Alloys of this type must be annealed for a long time for the determination of the solubility line and all methods are identical for this purpose, because for all of the methods the alloys must be in the equilibrium state.

In the second case the process of the decomposition on tempering the quenched alloys proceeds by sudden precipitation of the new phase from supersaturated solid solution and by changing it into the equilibrium state, passing over the intermediate composition. This can be shown for silver-copper alloys microscopically (Fig. 10 and pp. 108-109) and with X-rays.<sup>28</sup> With X-rays the lattices of both solid solutions present at once in alloy can be observed and, with the help of lattice dimension, the composition of these solid solutions can be determined. In this case, after short annealing at different temperature the concentration of the saturated solid solutions at these temperatures can be determined with X-rays, without reaching the equilibrium state at all parts of specimens of alloy.

For X-ray determination of the solubility line in silver-copper alloys it is not necessary to place the specimens in full equilibrium state, it is sufficient if the process of decomposition is just commenced. All operations of quenching and tempering for X-ray determination of the solubility line can be made on specimens of only one chemical composition. These two facts are the reasons why I find the X-ray method superior for the determination of solubility line of silver-copper alloys.

K. R. VAN HORN, Cleveland, Ohio (written discussion).--The excellent and concurring investigations by Aggeew, Hansen and Sachs, by Stockdale and by Smith and Lindlieff have indicated that the decomposition of the supersaturated alpha solid solution of the copper-silver alloys is a most interesting one.

Smith and Lindlieff gave curves which showed a relatively small increase in hardness and tensile strength of the copper-rich alloys on aging. An unusual effect was noted in that maximum hardness occurred at a point where the tensile strength had decreased appreciably below that of the quenched alloy. Dr. Mehl has offered a possible explanation of the inability of the alloys to harden on the precipitation of the silver solid solution. There are a few other possibilities which might be interesting to consider at this time.

Smith and Lindlieff's curves which show the effect of reannealing on the properties of a 4.95 per cent silver alloy quenched from 750° C. included only values for treatments of 300° C. and above. The high temperature of the treatments and the relatively long period of the anneal (4 hr.) might suggest that appreciable hardening did not occur because the silver solid solution precipitate had attained supercritical particle size. Smith and Lindlieff doubt this possibility because of the low conductivity of the quenched alloys and the fact that quenching rates up to one minute or slightly more had little effect. It can be recalled that the conductivity of aluminum alloys of the duralumin type, on aging at room temperature, actually decreases, and this is

<sup>28</sup> Reference of footnote 1.

accompanied by an increase in hardness. The slight effect on hardness of variations in the quenching rate might also indicate little change of the supercritical particle dimensions.

The temperature range from 25° to 300° C. has been shown to be very important in the tempering or artificial aging of many ferrous and nonferrous alloys. Aging treatments at 250° C. and above generally produce an "overaged" condition in the aluminum alloys which are susceptible to precipitation-hardening. The much discussed blue-brittleness range (200° to 350° C.) of low-carbon steels has frequently been attributed to the precipitation of iron oxides, carbides and nitrides. The hardness of quenched high-carbon and tool steels is increased before the usual decrease by the critical dispersion of cementite particles precipitated at temperatures from 100° to 250° C. Determination of the properties of the copper-rich alloys after treatments at 100° and 200° C. might prove interesting, and yet may not show a pronounced increase in hardness.

The room-temperature hardening of duralumin is generally ascribed to the presence of a vast number of very small, hard particles dispersed through the plastic grains of aluminum containing some copper in true solid solution. Maximum hardness is consummated when the precipitated phase is relatively hard; *i. e.*, intermetallic compounds or inclusions possessing low symmetry. We should not expect that the relatively soft face-centered cubic silver solid solution would produce hardening comparable to that effected by an intermetallic compound. The known inherent softness of the precipitating silver phase might be a feasible explanation of the absence of marked aging of the copper-silver alloys.

Some of the characteristics of the copper-rich copper-silver alloys observed by Smith and Lindlieff, and by Ageew, Hansen and Sachs, have suggested that precipitation in these alloys might be analogous to the aluminum-silicon system. Aluminum-silicon alloys are considered relatively soft in comparison with the so-called strong aluminum alloys. Hardness comparable to that effected by the critical dispersion of  $Mg_2Si$ ,  $Mg_3Al_2$  and  $CuAl_2$  is never approached by silicon, which varies in solid solubility from 0.05 per cent at room temperature to 1.65 per cent at 577° C. Modification of the aluminum-silicon alloys by alkali metals or rapid cooling decreases the liquidus representing primary silicon separation, lowers the eutectic temperature and increases the silicon eutectic concentration. These and other unusual characteristics indicate that it is extremely difficult for silicon nuclei to form. Migration of the large silicon atoms through the aluminum lattice is very slow. When sufficient mobility is attained by a higher annealing temperature, nuclei form and attract atoms from wide areas causing the silicon to cluster and coalesce into large particles. Consequently precipitation-hardening in the aluminum-silicon alloys is not realized because of the inability of the solute silicon atoms to form nuclei readily and, when sufficient impetus is attained, rapid clustering and segregation takes place, resulting in overaging.

It is entirely possible that a similar mechanism might explain the observed data in the copper-silver system. The silver atom is large and diffusion at low temperatures would be slow. This condition inhibits nucleus formation, but when nuclei are created the silver atoms would be rapidly attracted from a considerable distance, resulting in few but large particles and thus decreasing the resistance of the alloy to slip. The assumption gains additional emphasis from the demonstration by Ageew, Hansen and Sachs that precipitation does not occur gradually with a uniformly changing lattice parameter of the alpha solution, but very suddenly. Smith and Lindlieff microscopically show the sudden precipitation by very localized areas containing the dispersed phase adjacent to unaltered grains.

C. S. SMITH (written discussion).—It is much to be hoped that Dr. Mehl will be able to continue his studies of the precipitation mechanism in this and other systems, for his method of attack is one which is likely to prove a most fruitful one.

Dr. Stockdale's excellent work on the constitution of various alloy systems is so well known that his critical comments are particularly valuable. The agreement rather than the slight differences between his work and ours should be emphasized. Only very accurate future work will show which of the two diagrams is more nearly correct. In the absence of definite data, it is difficult to see how 0.015 per cent oxygen could replace 0.3 per cent silver, although this is by no means impossible. Regarding the approach to equilibrium at low temperatures, the fact that the first appearance of patches of precipitate as shown in Fig. 10 is very rapid should not mask the fact that final precipitation takes place peculiarly slowly. Indeed, even after 408 hr. at 400° C. (Fig. 11), precipitation seems to be by no means complete, if we accept the indications of X-ray examination that the unprecipitated patches are still of the original composition and supersaturated with silver.

We fully appreciate the advantages, pointed out by Dr. Ageew, of using X-ray diffraction methods in the determination of equilibrium diagrams, particularly of such systems as the present in which sudden decomposition occurs, and in any system at low temperatures where diffusion is so slow that particles large enough for certain microscopic identification are produced only after extremely long annealing periods. Nevertheless, it has never been shown that true equilibrium as shown by X-ray methods is reached in the copper-silver alloys in 3 to 5 hr. To prove this it would be necessary to show that the final lattice parameter after a very lengthy anneal agreed with that produced in the first few hours. Considerable caution should be exercised, particularly when studying alloys quenched from high temperatures, for it is never certain how much decomposition occurs during cooling. In the case of quenched alloys, the extreme sensitivity of the X-ray method is a disadvantage, for while an observer with the microscope can readily detect and discount for decomposition occurring during cooling, the X-ray diffraction pattern necessarily shows those phases actually existing in the sample at room temperatures, and does not indicate which may have resulted from partial decomposition during cooling. When the diffraction studies are made actually at high temperatures, this objection, of course, disappears completely.

Dr. Van Horn's suggestion that precipitation in the silver-copper alloys has already passed a maximum at 300° C. is not in agreement with the facts. Complete hardness curves preceded the annealing for the tensile tests described in the paper and have lately been repeated with greater accuracy. There is some change resulting in a slight increase in hardness after a 4-hr. annealing at 200° to 250° C., but the main increase does not occur until visible pearlitic precipitation commences at 300° C. The hardness reaches a broad maximum at 400° to 500° C. corresponding to almost complete visible precipitation and the minimum tensile strength, while beyond 550° C. it drops rapidly to approach the original hardness of the quenched alloy. There is, however, a factor which results in rather variable hardness of the alloys and tends to mask the increase at 200° C. This is the quenching rate, which is more important than the statement in the paper (p. 113) indicates and renders it impossible to obtain uniform hardness throughout a quenched specimen of appreciable size, although the lack of uniformity disappears on specimens annealed to maximum hardness. A perfectly quenched silver-copper alloy containing 5 per cent silver showed no change in hardness during two months at room temperature and there is nothing to indicate that it is not perfectly stable.

# Equilibrium Relations in Aluminum-copper-magnesium and Aluminum-copper-magnesium Silicide Alloys of High Purity

By E. H. DIX, JR.,\* G. F. SAGER,† AND B. P. SAGER,‡ NEW KENSINGTON, PA.

(New York Meeting, February, 1932)

THE work of Merica<sup>1</sup> and other investigators indicates that the phenomenon of age-hardening in alloys of the duralumin type is primarily dependent upon the variation in the solubility of copper with temperature. In addition to copper, however, these alloys contain small amounts of magnesium, silicon, manganese and iron, which may affect the age-hardening either directly or indirectly. The effect of these elements on the solubility of copper and on the manner in which this solubility varies with the temperature is of considerable interest, therefore. The effect of magnesium is of especial interest because apparently it exerts a marked effect on the natural or room-temperature aging of alloys of the type described.<sup>2</sup>

A series of investigations<sup>3</sup> has been in progress in the research laboratories of the Aluminum Company of America to determine the functions

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<sup>1</sup> P. D. Merica, R. G. Waltenberg and H. Scott: Heat Treatment of Duralumin. U. S. Bur. Stds. *Sci. Paper* 347 (1919).

<sup>2</sup> M. Gayler: Constitution and Age-Hardening of Alloys of Aluminum with Copper, Magnesium, and Silicon in the Solid State. *Jnl. Inst. Met.* (1922) 28, 213.

W. Fraenkel: Vergütbare Aluminiumlegierungen. *Ztsch. Metallkunde.* (1920) 12, 427.

<sup>3</sup> E. H. Dix, Jr.: Note on the Microstructure of Aluminum-Iron Alloys of High Purity. *Proc. Amer. Soc. Test. Mat.* (1925) 25, Pt. 2, 120.

E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans. A. I. M. E.* (1926) 73, 560.

E. H. Dix, Jr. and W. D. Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc. Inst. Met. Div., A. I. M. E.* (1927) 315.

E. H. Dix, Jr. and A. C. Heath, Jr.: Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. *Proc. Inst. Met. Div., A. I. M. E.* (1928) 164.

E. H. Dix, Jr. and F. Keller: Equilibrium Relations in Aluminum-magnesium Alloys of High Purity. *Proc. Inst. Met. Div., A. I. M. E.* (1929) 351.

E. H. Dix, Jr., F. Keller and R. W. Graham: Equilibrium Relations of Aluminum-magnesium-silicide Alloys of High Purity. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 404.

W. L. Fink and K. R. Van Horn: Constituents of Aluminum-iron-silicon Alloys. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 383.



of the various elements contained in such alloys. All of the alloys employed in these investigations were prepared from electrolytically refined aluminum.<sup>4</sup> Equilibrium relations in high-purity alloys of aluminum and copper, to approximately 6 per cent of the latter constituent, have previously been investigated by Dix and Richardson. The present investigation was undertaken to determine the individual effects of small additions of magnesium and magnesium silicide on the above relations with especial reference to the effect on the solubility of copper. It was hoped that this information would throw more light on the roles played by magnesium and magnesium silicide in certain of the strong aluminum alloys.

Conventional methods were employed in the determination of the solidus and solid solubility of copper. In determining the solidus, specimens were first annealed to insure homogeneity, then raised to and quenched from various elevated temperatures and examined microscopically for evidences of melting. In determining the solubility curve, specimens heat-treated so as to insure equilibrium at various temperatures were quenched from those temperatures and examined for excess constituent.

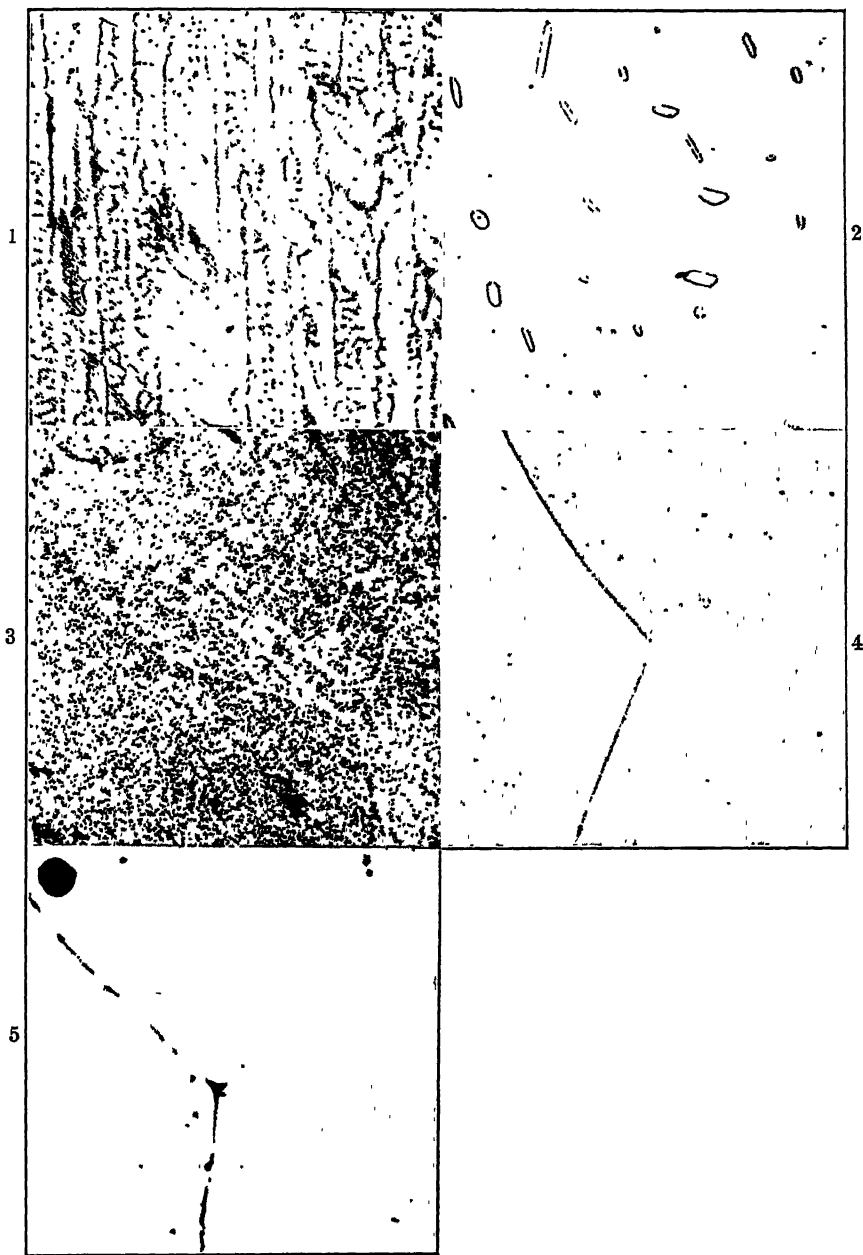
The alloys were prepared in crucibles of Acheson graphite, using a small electric crucible furnace. The aluminum was melted first and the copper and magnesium silicide added in the form of hardeners. The magnesium was introduced in the form of sticks shortly before pouring. The analyses of the materials used in preparing these alloys are given in Table 1. To prevent the oxidation of the magnesium, it was held below the surface by a graphite rod. The melts were stirred vigorously and carefully skimmed previous to pouring. All alloys were chill-cast in a horizontal open-type cast-iron mold of small section. The rapid solidification which resulted reduced segregation to a minimum. Figs. 1 and 7 illustrate typical cast structures.

TABLE 1.—*Chemical Compositions of Materials*

Material	Composition, Per Cent						
	Cu	Mg	Si	Fe	Mn	Ti	Al
Aluminum.....	0.02		0.009	0.005		0.004	99.96 <sup>a</sup>
Magnesium.....	0.00	99.98 <sup>a</sup>	0.00	0.00			0.01
(Other group II metals, 0.01)							
Aluminum-copper.....	31.82		0.02	0.04	0.00	0.003	68.12 <sup>a</sup>
Aluminum-magnesium-silicide.....	0.02	20.15	11.83	0.10	0.01		67.84 <sup>a</sup>

<sup>a</sup> By difference.

<sup>4</sup> F. C. Frary: Electrolytic Refining of Aluminum. *Trans. Amer. Electrochem. Soc.* (1925) 47, 275.



FIGS. 1-3.—ALUMINUM ALLOY (3.95 PER CENT CU, 0.52 PER CENT MG).

Fig. 1. Chill-cast in iron mold. Etched with 0.5 per cent HF.  $\times 100$ .

Fig. 2. Heat-treated 5 days at  $530^{\circ}\text{C}$ ., cooled slowly to  $450^{\circ}\text{C}$ ., held 6 days and quenched. Etched with 0.5 per cent HF.  $\times 500$ . Shows coalesced particles of  $\text{CuAl}_2$ .

CAPTIONS CONTINUED ON NEXT PAGE.

## ALUMINUM-COPPER-MAGNESIUM SYSTEM

The ternary system aluminum-copper-magnesium has been investigated by Vogel<sup>5</sup> and Gayler.<sup>6</sup> The former investigated the constitution,

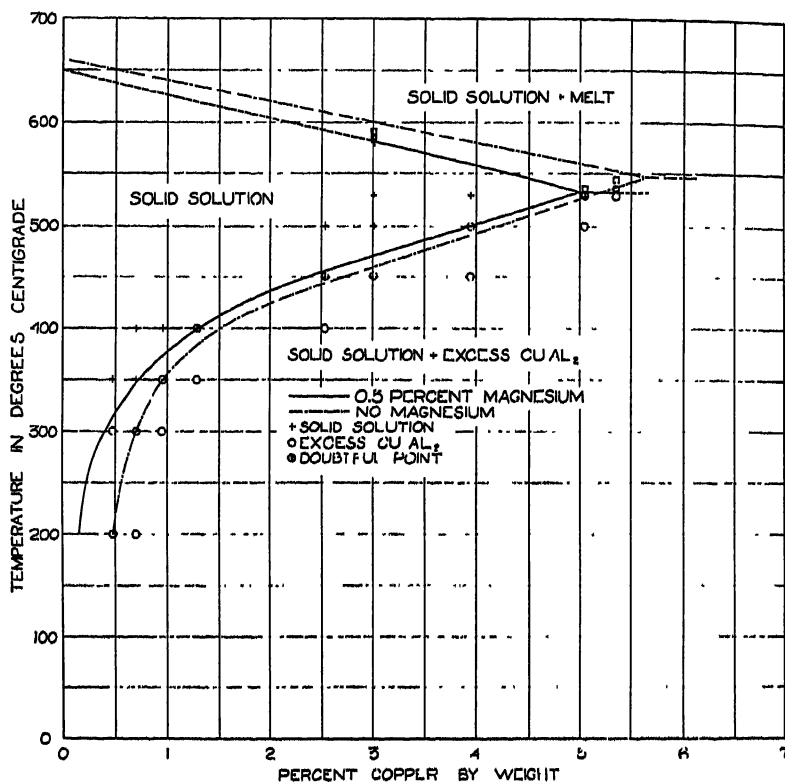


FIG. 6.—EQUILIBRIUM RELATIONS IN ALUMINUM-COPPER AND ALUMINUM-COPPER-MAGNESIUM SYSTEMS.

for temperatures above the solidus, of alloys in which both magnesium and copper varied from 0 to 50 per cent; while the latter dealt with the

<sup>5</sup> O. Vogel: Ternary Alloys of Aluminum with Magnesium and Copper. *Ztsch. f. anorg. Chem.* (1919) 107, 265-307.

<sup>6</sup> M. Gayler: The Constitution and Age-Hardening of the Ternary Alloys of Aluminum with Magnesium and Copper. *Jnl. Inst. Met.* (1923) 29, 507-528.

Fig. 3. Heat-treated 5 days at 530° C. and quenched. Reheated 41 days at 200° C. Etched with 0.5 per cent HF.  $\times 500$ . Shows finely dispersed particles of  $\text{CuAl}_2$ .

FIGS. 4-5.—ALUMINUM ALLOY (3.01 PER CENT Cu, 0.51 PER CENT Mg).

Fig. 4. Heat-treated 5 days at 530° C. and quenched. Reheated to 584° and quenched. Etched with 0.5 per cent HF.  $\times 500$ . Illustrates junction of three grains. Compare with Fig. 5.

Fig. 5. Heat-treated 5 days at 530° C. and quenched. Reheated to 594° and quenched. Etched with 0.5 per cent HF.  $\times 500$ . Illustrates melting at junction of three grains.

constitution, below the solidus, of alloys having compositions varying from 0 to 4 per cent copper and 0 to 12 per cent magnesium.

The compositions (by analysis) of the alloys examined in the present investigation are given in Table 2.

TABLE 2.—*Compositions of Aluminum-copper-magnesium Alloys*

Melt No	Copper, Per Cent	Magnesium, Per Cent
4508	0.49	0 50
4509	0.71	0 51
4510	0.96	0 51
4511	1.30	0 52
4512	2.54	0.50
4513	3.01	0.51
4514	3.95	0.52
4515	5.05	0 49
4516	5.35	0 50

To check the purity of the alloys, a more complete analysis was run on alloy M4516. In addition to copper and magnesium, it was found to contain 0.03 per cent Fe, 0.03 per cent Si, 0.00 per cent Mn and 0.00 per cent Ti.

A résumé of the heat treatments of the various specimens used in the solubility determinations is given in Table 3.

TABLE 3.—*Heat Treatment of Aluminum-copper-magnesium Alloys*

Equilibrium Temperature, Deg. C.	Heat Treatment
530	Heat-treated 5 days at 530° C. and quenched.
500	Heat-treated 5 days at 530° C., cooled to 500° in 1 day, held there 5 days, and quenched.
450	Heat-treated 5 days at 530° C., cooled to 500° in 1 day; held 5 days; cooled to 450° in a day; held 6 days and quenched.
400	Procedure through 450° C. same as above. After 6 days at 450° specimens were cooled to 400° in 3 days, held 8 days and quenched.
350	Procedure through 400° C. same as above. After 8 days at 400° specimens were cooled to 350° in 4 days, held 9 days and quenched.
300	Procedure through 350° C. same as above. After 12 days at 350° specimens were cooled to 300° in 4 days, held 9 days and quenched.
200	Specimens heat-treated 10 days at 500° C. and quenched. Reheated to 200° in a salt bath, held 41 days and quenched.

An etching reagent containing 0.5 per cent commercial hydrofluoric acid in water solution was used for removing surface flow from the polished specimens before metallographic examination. A magnification of 500 diameters was sufficient in most instances.

The results of the microscopic examination of the specimens listed in Table 3 are shown graphically in Fig. 6. For comparison, the solubility limit for binary aluminum-copper alloys, according to Dix and Richardson, is also included. The 0.5 per cent addition of magnesium slightly reduced the solid solubility of copper. The form of the curve is not greatly altered. As would be expected, the  $\text{CuAl}_2$  precipitated at lower temperatures is present in a more highly dispersed form than the large particles of constituent found in specimens annealed at more elevated temperatures; see Figs. 2 and 3.

In the investigation of the solidus, chill-cast specimens were annealed for 56 hr. at approximately  $530^\circ \text{C}$ . to produce homogeneity, then quenched. They were subsequently reheated to and quenched from various more elevated temperatures, after which microscopic examination for indications of incipient melting was made. This usually occurred at grain boundaries. Fig. 4 shows the microstructure of a specimen heated to several degrees below the solidus. No melting is apparent. Incipient melting is shown in Fig. 5.

A cooling curve taken on alloy M4516 (Cu 5.35, Mg 0.50 per cent) indicated a liquidus temperature of  $640^\circ \text{C}$ .

Since the majority of the strong aluminum alloys have copper contents ranging from 2 to 5 per cent, the small alteration in the solubility of that element would not appear to be of great significance. The influence of magnesium on the properties of these alloys may be the result of an effect which it exerts on the degree of dispersion or the precipitation rate. It must also be kept in mind that the effect of magnesium may be markedly altered by the presence of various strong alloy constituents.

#### ALUMINUM-COPPER-MAGNESIUM SILICIDE SYSTEM

Very few investigations of the aluminum-copper-magnesium silicide system have been published. The most thorough of these was by Gayler<sup>7</sup> who investigated the aluminum-rich end of this system and reported that the solid solubility of  $\text{CuAl}_2$  was greatly decreased by the presence of magnesium silicide. An addition of 0.7 per cent magnesium silicide appeared to reduce the solid solubility of  $\text{CuAl}_2$  from 4.5 per cent to 2 per cent at  $500^\circ \text{C}$ ., greater percentages having little further effect.

This investigation deals with a small corner of the Al-Cu-Mg-Si system. Magnesium and silicon were introduced in the proper ratio to form magnesium silicide, the concentration of that compound being kept

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<sup>7</sup> M. Gayler: Reference of footnote 2.

constant at 1.3 per cent in all alloys. A recent investigation at these laboratories<sup>8</sup> indicated that this addition was sufficient to saturate the solution at 500° C., the maximum heat-treating temperature employed in determining the solubility.

The alloys were prepared as described above. The impurities determined in the alloy of highest copper content were: Fe, 0.02 per cent; Mn, 0.00; Ti, 0.002. The compositions of the alloys are given in Table 4.

TABLE 4.—*Chemical Compositions of Aluminum-copper-magnesium Silicide Alloys*

Melt No.	Composition, Per Cent			Mg <sub>2</sub> Si, Calculated Per Cent	Excess Si, Calculated Per Cent
	Cu	Si	Mg		
4534	0.49	0.55	0.87	1.38	0.05
4535	0.73	0.53	0.86	1.36	0.03
4536	0.98	0.57	0.85	1.34	0.08
4537	1.50	0.57	0.87	1.38	0.07
4538	2.83	0.59	0.87	1.38	0.09
4539	3.05	0.60	0.83	1.31	0.12
4540	3.84	0.61	0.80	1.26	0.14
4541	4.82	0.58	0.83	1.31	0.10
4542	5.44	0.63	0.81	1.28	0.16

The heat treatment of the specimens used in the solubility determinations is indicated in Table 5.

TABLE 5.—*Heat Treatment of Aluminum-copper-magnesium Silicide Alloys*

Equilibrium Temperature, Deg. C.	Heat Treatment
500	Heat treated 10 days at 500° C. and quenched.
450	Heat treated 10 days at 500° C. and cooled to 450° in 20 days, held 16 days and quenched.
400	Heat treated 10 days at 500° C. cooled to 400° in 20 days, held 7 days and quenched.
350	Heat treated 10 days at 500° C. cooled to 350° in 30 days, held 9 days, and quenched.
300	Heat treated 10 days at 500° C. cooled to 300° in 43 days, held 16 days, and quenched.
200	Heat treated 10 days at 500° C. and quenched, reheated at 200° C. in a salt bath for 41 days and quenched.

The specimens used in determining the solidus were all annealed for 10 days at 500° C. to insure homogeneity, and quenched. They

<sup>8</sup> E. H. Dix, Jr., F. Keller and R. W. Graham: Equilibrium Relations in Aluminum-magnesium Silicide Alloys of High Purity. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 404.

were subsequently heated for approximately one-half hour at various more elevated temperatures and quenched.

In order to determine the solid solubility of copper, specimens annealed as shown in Table 5 were examined microscopically for excess  $\text{CuAl}_2$ . According to Gayler, the only constituents to be expected in this series of alloys are  $\text{CuAl}_2$  and  $\text{Mg}_2\text{Si}$ . On examination, however, a third constituent was observed. This constituent was gray in color and usually occurred as plates or needles; its amount appeared to increase with the copper content at the expense of the  $\text{Mg}_2\text{Si}$ . Since this constituent was not observed in the aluminum-copper-magnesium, aluminum-copper-silicon, or aluminum-magnesium silicide systems, it probably contains aluminum, copper, magnesium and silicon and will be referred to as Al-Cu-Mg-Si.<sup>9</sup>

It was very easy to recognize the  $\text{Mg}_2\text{Si}$ , which is slate to iridescent blue when unetched, the color depending on the method of polishing. The  $\text{CuAl}_2$  and Al-Cu-Mg-Si could easily be confused. Both are gray when unetched, Al-Cu-Mg-Si being somewhat darker in shade. The etching characteristics, however, are different. Hot 10 per cent nitric acid turns the  $\text{CuAl}_2$  brown, whereas the Al-Cu-Mg-Si constituent first becomes an iridescent blue and on further etching is entirely eaten out. When etched with a hot 10 per cent NaOH solution (70° C.) for 4 sec., the  $\text{CuAl}_2$  turns brown, the blue  $\text{Mg}_2\text{Si}$  is not attacked and Al-Cu-Mg-Si is outlined. Since a 0.5 per cent solution of hydrofluoric acid merely outlines both  $\text{CuAl}_2$  and Al-Cu-Mg-Si and since the hot nitric acid etch attacks vigorously both  $\text{Mg}_2\text{Si}$  and Al-Cu-Mg-Si, the hot 10 per cent NaOH etch was used on all specimens. When using this etch, it was easy to differentiate between the blue  $\text{Mg}_2\text{Si}$ , the brown  $\text{CuAl}_2$ , and the

<sup>9</sup> In previous publications from these laboratories the aluminum has been omitted from designations of this character. This practice has led to some misunderstandings, however, so constituents will henceforth be designated in the above manner.

FIG. 7.—ALUMINUM ALLOY (5.44 PER CENT Cu, 1.28 PER CENT  $\text{Mg}_2\text{Si}$ , 0.16 PER CENT EXCESS Si).

Chill-cast in iron mold. Etched with 0.5 per cent HF.  $\times 100$ .

FIG. 8.—ALUMINUM ALLOY (2.83 PER CENT Cu, 1.38 PER CENT  $\text{Mg}_2\text{Si}$ , 0.09 PER CENT EXCESS Si).

Heat-treated 16 days at 500° C., slowly cooled to 400°, held 17 days, and quenched. Unetched.  $\times 500$ . Shows light  $\text{CuAl}_2$  particles and somewhat darker Al-Cu-Mg-Si particles. Darkest particles are  $\text{Mg}_2\text{Si}$  and actually are blue.

FIG. 9.—SAME AREA AS SHOWN IN FIG. 8.

Etched with hot 10 per cent NaOH (70° C.).  $\times 500$ . Notice that this etch has darkened the particles of  $\text{CuAl}_2$  but has not appreciably altered the other two constituents shown in Fig. 8.

FIG. 10.—ALUMINUM ALLOY (3.05 PER CENT Cu, 1.31 PER CENT  $\text{Mg}_2\text{Si}$ , 0.12 PER CENT EXCESS Si).

Heat-treated 16 days at 500° C., slowly cooled to 450°, held 16 days and quenched. Etched with 0.5 per cent HF.  $\times 500$ . Shows light particles of  $\text{CuAl}_2$  and darker particles of Al-Cu-Mg-Si.

FIG. 11.—ALUMINUM ALLOY (2.83 PER CENT Cu, 1.28 PER CENT  $\text{Mg}_2\text{Si}$ , 0.09 PER CENT EXCESS Si).

Heat-treated 16 days at 500° C., quenched and reheated 41 days at 200°. Etched with 10 per cent cold NaOH.  $\times 500$ . Shows finely dispersed particles of  $\text{CuAl}_2$ , dark coalesced particles of  $\text{Mg}_2\text{Si}$  and large gray particles of coalesced Cu-Mg-Si.



FIGS. 7-11.—CAPTIONS ON OPPOSITE PAGE



outlined Al-Cu-Mg-Si, which appears white in the cream colored matrix. Fig. 8 illustrates the three constituents when unetched. Fig. 9 shows the same area after a 4-sec. etch with a hot solution of 10 per cent NaOH (70° C.). The large particle of Al-Cu-Mg-Si appears lighter after etching because of the darker matrix. The light  $\text{CuAl}_2$  particles bordering the  $\text{Mg}_2\text{Si}$  at the center left and top have been turned brown by the etch, as have other  $\text{CuAl}_2$  particles in this area. The  $\text{Mg}_2\text{Si}$  is blue before and after etching. Fig. 10 illustrates  $\text{CuAl}_2$  and Al-Cu-Mg-Si. The specimen was etched with a 0.5 per cent solution of hydrofluoric acid in order to outline the constituents. The color of neither constituent has been appreciably changed by the etch. Figs. 8, 9 and 10 illustrate specimens annealed at temperatures sufficiently high for the constituents to agglomerate to fairly large particles. Fig. 11 illustrates a specimen containing 2.83 per cent copper annealed 10 days at 500° C. and reheated 41 days at 200° C. At 500° C. the  $\text{CuAl}_2$  is completely in solution whereas the  $\text{Mg}_2\text{Si}$  and Al-Cu-Mg-Si are out of solution as fairly large particles. When reheating at 200° C. the  $\text{CuAl}_2$  precipitates in a very finely dispersed form. The large particles of blue  $\text{Mg}_2\text{Si}$  and the light particles of Al-Cu-Mg-Si stand out in a background of finely dispersed  $\text{CuAl}_2$  in an aluminum matrix.

The temperature at which the eutectic valley intersects the section under investigation was determined by running cooling and heating curves on melt 4541 (4.82 per cent copper) using the procedure employed in previous investigations at this laboratory.<sup>10</sup> The break in both the heating and cooling curves was at 510.5° C.

The results of the examination are shown graphically in Fig. 12. The solid solubility curves for  $\text{CuAl}_2$  and Al-Cu-Mg-Si, as well as the solidus for this system, are represented by solid lines. Although the addition of  $\text{Mg}_2\text{Si}$  does not appear to have altered appreciably the apparent solubility of copper (the difference in Fig. 12 is within experimental error) it is probable that the use of copper in the formation of Al-Cu-Mg-Si has compensated for a decrease in the solubility of that element.

In order to establish whether the above-mentioned gray constituent (Al-Cu-Mg-Si) was actually a new phase, an experiment was made to determine whether it was possible to introduce still another phase by preparing an alloy of the same type but containing silicon in excess of the ratio in the compound  $\text{Mg}_2\text{Si}$ . An alloy (M 7436) of the following composition was prepared: Cu, 2.86 per cent; Mg, 0.86; Si, 1.08.

This alloy was heated 8 days at 500° C., cooled over a period of 13 days to 450° C., held at this temperature for 3½ days and quenched. Microscopic examination showed only  $\text{CuAl}_2$ , Al-Cu-Mg-Si and free

<sup>10</sup> E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans. A.I.M.E.* (1926) **73**, 560.

silicon out of solution. In an alloy containing 2.5 per cent copper and 1.4 per cent  $\text{Mg}_2\text{Si}$  it was found that  $\text{Mg}_2\text{Si}$ ,  $\text{CuAl}_2$  and  $\text{Al-Cu-Mg-Si}$  coexisted at  $400^\circ\text{C}$ . The disappearance of  $\text{Mg}_2\text{Si}$  with an increase of the silicon content is in accord with the phase rule, since, except at invariant points, no more than four phases can coexist in a four-component system.

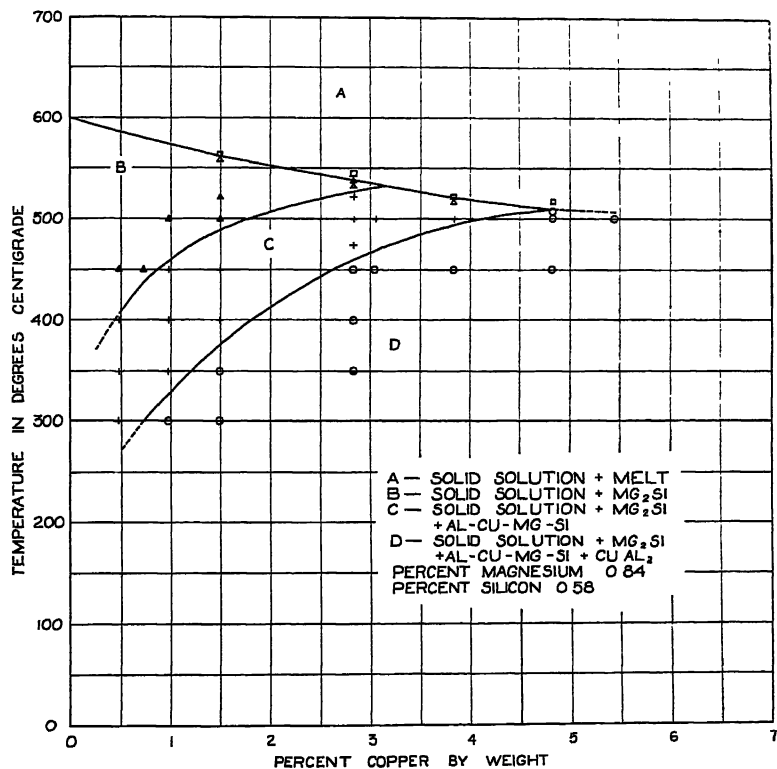


FIG. 12.—EQUILIBRIUM RELATIONS IN ALUMINUM-COPPER-MAGNESIUM-SILICON SYSTEM.

Contrary to the results reported by Gayler,<sup>11</sup> the addition of approximately 1.3 per cent  $\text{Mg}_2\text{Si}$  to aluminum-copper alloys does not decrease the apparent solubility of copper to any appreciable extent. It is possible, however, that some decrease in solubility does occur but is compensated by the formation of  $\text{Al-Cu-Mg-Si}$ .

#### ACKNOWLEDGMENT

The authors desire to express their appreciation to Mr. A. C. Heath for his preliminary work in this investigation and Mr. H. V. Churchill, under whose direction the chemical analyses were made.

<sup>11</sup> M. Gayler: Reference of footnote 2.

## DISCUSSION

(W. M. Peirce presiding)

M. L. V. GAYLER, Teddington, Middlesex, England (written discussion).—The paper by Mr. Dix and his colleagues is particularly interesting to me on account of the paper which Mr. Preston and I presented last March to the Institute of Metals, and we are glad that the authors' results regarding the effect of 0.5 per cent Mg on the solubility of copper in aluminum agrees with those which Mr. Preston and I deduced from our observations.

With regard to the ternary alloys, Al-Cu-Mg<sub>2</sub>Si, the authors have shown results which differ from those which I published in 1923, using aluminum which contained 0.16 per cent iron. The identification of a new phase by the present authors is extremely interesting; the question, however, arises, whether the same phase is formed when iron, which exists as an impurity in the aluminum, is present in the alloy. It is highly probable that such a compound is still formed, but the actual composition may be slightly altered.

With regard to Fig. 12, I think that this diagram needs consideration. The authors have called the system by two different names: (1) Al-Cu-Mg<sub>2</sub>Si system; (2) Al-Cu-Mg-Si system. The first case represents a ternary system where one component is a compound formed by the combination of two constituents. In these circumstances it may be justifiable to consider the equilibrium as that of a ternary system provided that there is no excess of the two components forming the compound. If this is the case, the diagram shown in Fig. 12 needs qualification.

The phase field *C* (Al solid solution + Mg<sub>2</sub>Si + Al-Cu-Mg-Si) cannot, according to the phase rule, be bounded by a sloping solidus, for there are four phases present (i. e., liquid + Al + Mg<sub>2</sub>Si + Al-Cu-Mg-Si) and, therefore, the solidus must be a horizontal line, indicating an invariant reaction. Furthermore, since the ternary system Al-Cu-Mg<sub>2</sub>Si is being considered, the four-phase field *D* (Al + Mg<sub>2</sub>Si + Al-Cu-Mg-Si + CuAl<sub>2</sub>) cannot represent equilibrium conditions; one of these phases must disappear. In this case I would suggest, in view of the authors' facts, that it is probable that Al-Mg-Cu-Si is formed at the expense of Mg<sub>2</sub>Si. If, on the other hand, the system is regarded as the quaternary system Al-Cu-Mg-Si, the diagram in Fig. 12 is difficult to interpret on the lines of the conventional equilibrium diagram.

I sincerely hope that the authors will extend their field of investigation in this same direction and not limit their researches to one proportion of Mg<sub>2</sub>Si only.

R. S. ARCHER, Milwaukee, Wis.—It seems to me that these two systems will be of especial interest in connection with Dr. Merica's address on The Age-hardening of Metals.<sup>12</sup> His theory of age-hardening has been of tremendous value in all fields of metallurgy, starting with duralumin. His first proposal was that the hardening was due to the precipitation of CuAl<sub>2</sub>. Since that time, the British, in particular, have questioned the nature of the precipitate and suggested that it was magnesium silicide. The present work on constitution, therefore, is distinctly of interest in connection with age-hardening of duralumin.

I would like to ask Mr. Dix whether in the aluminum-copper-magnesium system, they have found any indication of a complex aluminum-copper-magnesium constituent?

E. H. DIX, JR.—Not in the particular alloys that were dealt with in that series. We do know that there is such a constituent, aluminum-copper-magnesium, but not in the particular alloys covered.

<sup>12</sup> See page 13.

E. H. DIX, JR., G. F. SAGER and B. P. SAGER (written discussion).—We are glad that Dr. Gayler has called attention to the inconsistency between the title of the paper and the results of our investigation. When this research was first undertaken we believed it possible to consider aluminum-copper-magnesium silicide as a three-component system. The data available in the literature at that time and work that had been done at these laboratories on equilibrium relations in aluminum-magnesium silicide alloys indicated that the magnesium silicide could be considered as a single component. The results of the present investigation indicate that this is not the case, however, and it will be noted that the system is considered as a four-component one in the discussion at the bottom of page 128 and the top of page 129. The four phases observed in field *D* of Fig. 12 could not coexist in equilibrium in a three-component system. The data determining the solidus are somewhat meager, nevertheless it is quite evident that the part of that line that bounds field *C* (Al solid solution,  $Mg_2Si$  and Al-Cu-Mg-Si) is not horizontal, as it would have to be if the system were a ternary one. The fact that the addition of silicon in sufficient excess of the magnesium silicide ratio to an alloy in field *D* causes the magnesium silicide and not the aluminum-copper-magnesium-silicon constituent to disappear suggests that the latter constituent is, in some regions at least, the more stable. Evidence recently presented by Mehl, Barrett and Rhines<sup>13</sup> indicates that  $Al_3Mg_2$  may be precipitated from aluminum-magnesium silicide alloys. This also shows that it is not safe to consider magnesium silicide as a single component in dealing with aluminum alloys.

It is very difficult satisfactorily to represent graphically the equilibrium relations in a four-component system. However, the diagram in Fig. 12 does show the manner in which the binary aluminum-copper system is modified by combined additions of 0.84 per cent Mg and 0.58 per cent Si.

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<sup>13</sup> See page 129.

## Equilibrium Relations in Aluminum-zinc Alloys of High Purity

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CLEVELAND, OHIO

(New York Meeting, February, 1932)

ZINC is one of the effective elements introduced to enhance the strength of aluminum. This strengthening is principally attributable to the high solid solubility of zinc in aluminum and the pronounced variation of solubility with temperature. Consequently an accurate determination of the solid solubility curve is desirable.

The solid solubility relations have been studied by numerous investigators. Shepherd<sup>1</sup> first established the existence of a solid solution region at the aluminum end of the diagram ( $\gamma$  phase) by specific volume and microscopic determinations. Bauer and Vogel<sup>2</sup> published a constitutional diagram which showed the limits of solid solubility as determined by thermal and microscopic methods. Hanson and Gayler<sup>3</sup> presented the aluminum-zinc diagram which is now most generally accepted (Fig. 1). Chill-cast samples were given thermal treatments designed to obtain equilibrium conditions, quenched, and microscopically examined. The solubility was placed between 15 to 20 per cent at 60° C., 20 to 22 per cent at 140° C. and 36 to 38 per cent at 270° C. Sander and Meissner<sup>4</sup> decidedly modified the limits of the  $\gamma$  phase field of Hanson and Gayler's diagram by using similar methods on chill-cast specimens annealed for a shorter period of time. Tanabe,<sup>5</sup> utilizing dynamic hardness, electrical conductivity and dilatometric measurements of specimens at temperature, obtained values comparable to Hanson and Gayler's at room temperature, but appreciably lower at higher temperatures. Nishimura<sup>6</sup> concluded from age-hardening results of aluminum-zinc alloy chill castings, which had been quenched from 400° to 500° C., that the solubility of zinc in aluminum at room temperature is less than 5

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<sup>1</sup> E. S. Shepherd: Aluminum-Zinc Alloys, *Jnl. phys. Chem.* (1905) 9, 504.

<sup>2</sup> O. Bauer and O. Vogel: Aluminum-Zinc Alloys, *Int. Jnl. Metall.* (1916) 8, 101.

<sup>3</sup> D. Hanson and M. V. L. Gayler: A Further Study of the Alloys of Aluminum and Zinc. *Jnl. Inst. Met.* (1922) 27, 267.

<sup>4</sup> W. Sander and K. L. Meissner: Zur Kenntnis der Konstitution der Aluminium-Zinklegierungen. *Ztsch. f. Metallkunde* (1922) 14, 385.

<sup>5</sup> T. Tanabe: Studies in the Aluminum-Zinc System, *Jnl. Inst. Met.* (1924) 32, 415.

<sup>6</sup> H. Nishimura: On the Age-Hardening of Aluminum-Rich Al-Zn Alloys. *Mem. Kyoto Imp. Univ.* (1924) 3, 133.

per cent. However, the solubility values increased rapidly to about 19 per cent at the eutectoid temperature. Ishihara,<sup>7</sup> using electrical conductivity and dilatometric methods, obtained values approximating those of Bauer and Vogel. Tiedemann<sup>8</sup> employed tensile measurements of thoroughly annealed specimens which rendered a solubility of approximately 15.5 per cent zinc at 240°C. There are wide discrepancies in these results and a careful redetermination of the solubility curve is imperative.

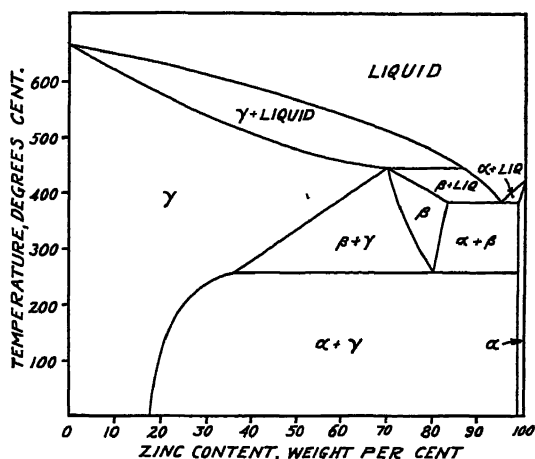


FIG. 1.—EQUILIBRIUM DIAGRAM OF ALUMINUM-ZINC SYSTEM. (Hanson and Gayler.)

The present report of the solubility relations below the eutectoid temperature in high-purity aluminum-zinc alloys is the tenth paper of a series<sup>9</sup> from the Laboratories of the Aluminum Company of America,

<sup>7</sup> T. Ishihara: On the Equilibrium Diagram of the Aluminum-Zinc-System. *Sci. Repts. Tohoku Imp. Univ.* (1925) 13, 427.

<sup>8</sup> O. Tiedemann: Zur Erforschung des Systems Aluminum-Zink. *Zisch. Metallkunde* (1926) 18, 18, 221.

<sup>9</sup> E. H. Dix, Jr.: Note on the Microstructure of Aluminum-iron Alloys of High Purity. *Proc. Amer. Soc. Test. Mat.* (1925) 25, Pt. 2, 120.

E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans. A. I. M. E.* (1926) 73, 560.

E. H. Dix, Jr. and W. D. Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc. Inst. Metal. Div., A. I. M. E.* (1927) 315.

E. H. Dix, Jr. and A. C. Heath, Jr.: Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. *Proc. Inst. Met. Div., A. I. M. E.* (1928) 164.

E. H. Dix, Jr. and F. Keller: Equilibrium Relations in Aluminum-magnesium Alloys of High Purity. *Proc. Inst. Metals Div., A. I. M. E.* (1929) 351.

E. H. Dix, Jr., F. Keller and R. W. Graham: Equilibrium Relations of Aluminum-magnesium Silicide Alloys of High Purity. *Trans. A. I. M. E., Inst. Metal. Div.* (1931) 404.

E. H. Dix, Jr., F. Keller and L. A. Willey: Equilibrium Relations in Aluminum-antimony Alloys of High Purity. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 396.

presenting the results of the investigation of equilibrium relations in aluminum-base alloys made from electrolytically refined aluminum.<sup>10</sup>

It seemed desirable, in view of the previous discordant results, to determine the solid solubility of zinc in aluminum by more than one experimental procedure. Hardness, electrical conductivity, microscopic and X-ray methods were used.

### HARDNESS MEASUREMENTS

Brinell hardness measurements were made on  $\frac{1}{4}$ -in. chill-cast slabs containing 1 to 34 per cent of C.P. zinc in electrolytically refined aluminum, which had been thoroughly homogenized at 500° to 550° C. Specimens were tested immediately after quenching from the homogenizing treatment and after subsequent thermal treatments. Quenched samples containing 5 per cent or more of zinc were found to harden on aging at room temperature. These results indicate that the solid solubility of zinc is less than 5 per cent at room temperature, assuming that hardening in aluminum-zinc alloys is produced by precipitation.

FIG. 2.—METHOD OF PLOTTING HARDNESS VALUES TO DETERMINE SOLID SOLUBILITY.  
A. Brinell hardness of alloys heated at 500° C.  
B. Brinell hardness of alloys heated at 250° C.  
C. Brinell hardness of alloys heated at 200° C.

of freshly quenched specimens is plotted against composition. Fig. 2 illustrates the anticipated relations. The slopes of the curves are functions of the hardening effected by the atoms in the solid solution and the hardness of the precipitating phase. The experimental data plotted in this manner yielded three curves, which were not coincident in the solid solution range and consequently could not be used to determine the solubility limits. The discrepancies were larger than might

W. L. Fink and K. R. Van Horn: Constituents of Aluminum-iron-silicon Alloys. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 383.

W. L. Fink, K. R. Van Horn and P. M. Budge: Constitution of High Purity Aluminum-titanium Alloys. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 421.

<sup>10</sup> F. C. Frary: Electrolytic Refining of Aluminum. *Trans. Amer. Electrochem. Soc.* (1925) 47, 275.

be expected from possible experimental errors in the Brinell readings. In the second method, where the increase in hardness or the hardness number of aged specimens is plotted against the composition, the uncertainties of the hardening mechanism are introduced. However, if it were assumed that maximum increase in hardness on aging corresponds to the solubility limit, the values of approximately 11 and 13 per cent zinc at 200° and 250° C., respectively, were obtained.

### ELECTRICAL CONDUCTIVITY MEASUREMENTS

Electrical conductivity can be measured with greater accuracy than hardness, and consequently it was thought that the solubility relations could be more definitely determined. A series of chill-cast aluminum-zinc alloy ingots (4 by 3½ by ¾ in.), the compositions of which are listed in Table 1, was preheated for 17 hr. at 500° C. and hot-rolled to ¼-in.

TABLE 1.—*Analyses of Alloys*

Alloy No.	Composition, Per Cent			
	Zn	Si	Fe	Cu
4003	3.00	0.005	0.007	0.007
4004	3.99			
4005	4.96			
4006	5.96			
4007	6.91			
4008	7.81			
4009	8.98			
4010	9.81			
4011	10.93			
4012	11.70			
4013	12.73			
4014	13.73			
4015	14.83			
4016	15.85			
4017	16.76			
4018	17.63			
4019	18.60			
4020	19.80	0.005	0.007	0.007

thick slabs. The slabs were homogenized at 500° C. for four days, quenched in cold water, aged at 150° C. for 24 hr. and cold-rolled to 22-gage sheet (0.025 in.). The conductivity specimens (20.5 by 0.75 by 0.025 in.) were milled from the sheets. The specimens were suspended in a heavy aluminum block in a Leeds & Northrup Homo-Furnace and annealed at 200° and 250° C. for various periods, ranging from 3 to 19 days.



The electrical conductivity was determined by measuring the drop in potential across the specimen, which was maintained at 25° C. in an oil thermostat, and across a standard resistance which was connected in series. A Leeds & Northrup type K potentiometer was used in the experiments.

It was discovered that room-temperature aging was sufficiently rapid to require an individual quench and an immediate measurement of each specimen. The conductivity values were approximately equal for the different annealing periods at either 200° or 250° C. However, the experimental points obtained in duplicate determinations deviated from the curves to such an extent that in some cases the exact locations of the dis-

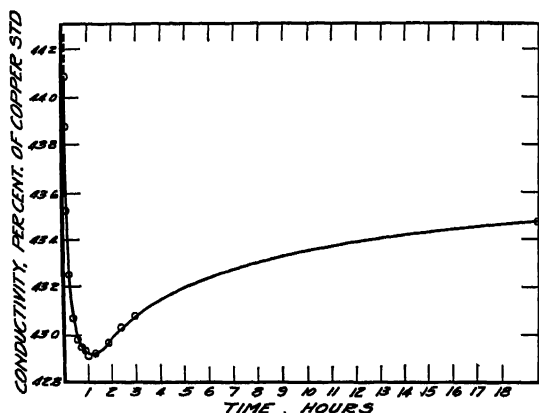


FIG. 3.—AGING AT 25° C. OF A 12.73 PER CENT ZINC ALLOY AFTER QUENCHING FROM 200° C.

continuities were somewhat in doubt. The results, however, would indicate that the zinc solubility is about 10 to 11 and 13 to 14 per cent at 200° and 250° C., respectively. It seemed that the variations might be attributed to differences in the aging rate and the time interval between quenching the specimen and measuring the conductivity. The velocity of aging is illustrated in Fig. 3, which gives the change of the electrical conductivity of a 12.73 per cent Zn sample which had been quenched from 200° C. Considerable aging occurs between quenching and measuring, for which no correction can be applied because an accurate extrapolation of the curve to zero time is obviously impossible.

If the samples are aged until the conductivity attains a constant value, a substantially different solubility limit is indicated. Fig. 4 compares the curve obtained 3 min. after quenching with that of the same specimens after aging 40 days at room temperature.

Attempts to determine the solid solubility of zinc in aluminum by measuring the electrical conductivity or any property of quenched speci-

mens at room temperature would be vitiated by immediate room-temperature aging. This factor and the inherent inaccuracies in measuring the Brinell hardness of relatively soft solid solutions ( $\gamma$  and  $\alpha$  phases) probably explain the variations observed in the hardness curves of quenched specimens.

### MICROSCOPIC EXAMINATION

Previous investigators, employing microscopic examination of quenched specimens, have obtained inconsistent solid solubility relations which may be attributed to either incomplete equilibrium or inability to detect the  $\alpha$  phase. However, this method was tried again because it would, in all probability, not be affected by room-temperature precipitation, because of the submicroscopic size of the reprecipitated particles.

Samples containing from 10 to 20 per cent Zn were clipped from the ends of the conductivity specimens and annealed for various periods (3 to 32 days) at 250° C. There seemed to be minute particles along the grain boundaries of the samples with higher zinc contents, but no etch was found that would reveal them without the formation of minute etching pits from which they were not definitely distinguishable. Consequently microscopic analysis was not continued on specimens quenched from lower temperatures, which are less conducive to the coalescence of the precipitate.

It is believed that some of the experiments just described give indications of the solid solubility at room temperature, 200° and 250° C., but no reliable quantitative values. Measurements *at temperature* of physical properties such as tensile strength, electrical conductivity, specific volume or lattice parameter, as well as the X-ray detection of the excess solute, should give a more accurate result by eliminating errors introduced by room-temperature precipitation. Revealing the excess zinc by the X-ray method was selected because the precipitation at room and other low temperatures is accelerated by cold working incident to the preparation of powdered specimens. This affects equilibrium which could not otherwise be realized at low temperatures.

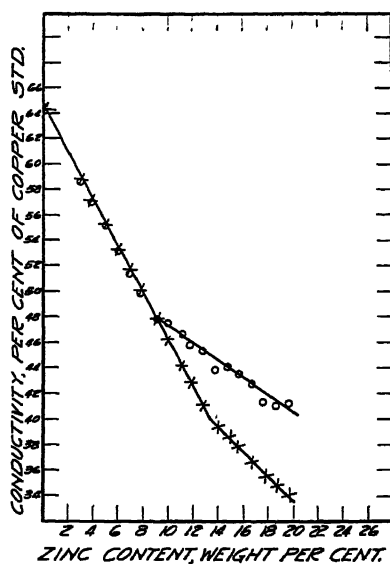


FIG. 4.—EFFECT OF ROOM-TEMPERATURE AGING ON CONDUCTIVITY OF ALUMINUM-ZINC ALLOYS QUENCHED FROM 250° C.

X. Conductivity of freshly quenched specimens.

O. Conductivity of specimens aged for 40 days after quenching.

## DETERMINATION OF SOLID SOLUBILITY RELATIONS BY X-RAY METHODS

*Apparatus.*—The diffraction patterns were made on a General Electric apparatus equipped with a molybdenum target tube operating at 30,000 volts and 20 milliamperes. A standard G.E. cassette containing a zirconium oxide filter was used in determining the room-temperature solubility. Another similar cassette, for higher temperatures, was remodeled to include a small electric resistance furnace, as shown in Fig.

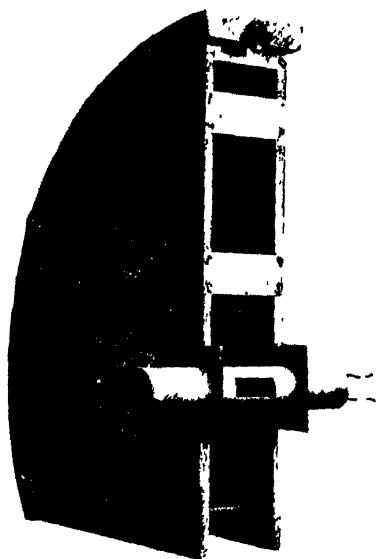


FIG. 5.—X-RAY CASSETTE EQUIPPED WITH FURNACE FOR MAKING DIFFRACTION PATTERNS AT TEMPERATURE.

5. The furnace could be properly aligned in both the horizontal and vertical direction by adjusting the supports in which oversized holes were drilled.

The furnace<sup>11</sup> consisted of an aluminum tube approximately 6 in. long by 0.75 in. inside diameter, two concentric fused silica tubes at either end, which centered the specimen, and coils of nichrome wire, embedded in the aluminum cement, which filled the space between the tubes. A rectangular opening through the furnace permitted the passage of the X-ray beam. The temperature was maintained at the desired point by a 30-gage chromel-X-copel thermocouple, the bead of which was in contact with the middle of the specimen, and a Hoskins type R. M. controller. An external resistance in the heating circuit regulated the power input at the optimum value. Heat loss was reduced to a minimum by suitable asbestos insulation around the furnace.

*Experimental Procedure.*—The X-ray samples were prepared from thoroughly homogenized 22-gage cold-rolled sheet, which was sheared from sections adjacent to the conductivity specimens. The samples were powdered by filing, passed through a 300-mesh screen, placed in thin-walled Pyrex capillary tubes 6 in. long and 0.04 in. outside diameter, and hermetically sealed. A series of specimens containing 3.00 to 19.80 per cent Zn for measurement at temperature was annealed for 7 to 12 days in an oil thermostat at the various temperatures to be investigated (100°, 150°, 200° and 250° C.). Each sample was transferred directly from the thermostat to the X-ray furnace, which was maintained at the same

<sup>11</sup> W. M. Peirce, E. A. Anderson and P. Van Dyck: *Jnl. Franklin Inst.* (1925) 200, 349.

temperature, and exposed for 48 hr., using Eastman Diafax films. The specimens aged at room temperature were similarly exposed. The conditions of exposure and development were maintained constant at values which preliminary experiments had shown to be optimum for detecting a phase that is present in a small quantity. This permitted a direct comparison of all films of the solubility specimens and synthetic standards prepared by mixing definite proportions of 300-mesh C.P. zinc and powdered electrolytically refined aluminum.

The diffraction patterns of the different alloys at each temperature were carefully examined for the reflections which represented the zinc lattice. For a constant temperature, the intensities of these reflections decreased with the zinc content until a concentration was reached at which only the most intense lines of the  $\alpha$  constituent were perceptible and below which these reflections could not be detected. The intensities of the zinc solid solution reflections at this concentration were compared with the zinc lines in the patterns of the synthetic standards which contained 0.5,<sup>12</sup> 0.6 and 0.75 per cent Zn. The zinc content of the standard producing zinc constituent lines of the same intensity as this sample was subtracted from this concentration to obtain the solubility limit at the temperature under consideration.

## RESULTS AND DISCUSSION

Duplicate determinations by the X-ray method at different temperatures and for various aging periods gave identical results, indicating that even at room temperature equilibrium is rapidly attained in specimens powdered from cold-rolled sheet, and that the method is capable of giving reproducible results. However, it is assumed that the severe cold working has not displaced the equilibrium, but has merely accelerated the precipitation. Moreover, the accuracy of the correction may be influenced by the relative size of the zinc particles in the standards and the  $\alpha$  solution in the solubility samples.

The solubility limits so determined are presented in Table 2, and compared in Fig. 6 with the results that have been obtained by the

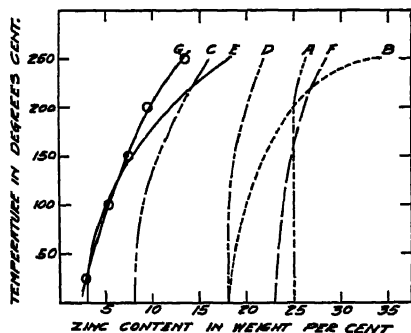


FIG. 6.—SOLID SOLUBILITY OF ZINC IN ALUMINUM ACCORDING TO PREVIOUS INVESTIGATORS.

- A. Bauer and Vogel
- B. Hanson and Gayler
- C. Tiedemann: Sander and Meissner
- D. Tanabe
- E. Nishimura
- F. Ishihara
- G. Fink and Van Horn, present investigation

<sup>12</sup> This is the most dilute standard that will give definite zinc reflections.

various investigators. The curve determined in the present investigation by the X-ray method is in good agreement from 25° to 150° C. with that of H. Nishimura. It should also be noted that the isolated results from the experimental hardness and electrical conductivity determinations approximate the corresponding values of Table 2.

TABLE 2.—*Solubility of Zinc in Aluminum*

TEMPERATURE, DEG. C.	ZINC CONTENT, PER CENT
25	2.7
100	5.2
150	7.4
200	9.4
250	13.4

## ACKNOWLEDGMENT

The authors wish to express their appreciation to Mr. L. A. Willey, who made the electrical conductivity measurements and microscopic examination, and to Mr. C. M. Tucker, who made the diffraction patterns. Their meticulous work made this publication possible.

## DISCUSSION

(*W. M. Peirce presiding*)

G. P. DE FOREST, New York, N. Y.—Is it absolutely necessary that equilibrium be attained in the X-ray method? It would seem to me that if there were any precipitation at all the X-ray method ought to show that up, even though perfect equilibrium were not attained.

K. R. VAN HORN, Cleveland, Ohio (written discussion).—A sensitive X-ray apparatus capable of accurately determining the lattice parameter would not require complete equilibrium for solid solubility measurements. The state of equilibrium as well as the solid solubility could be obtained from the variation in the dimensions of the unit cell of aluminum. However, in this experiment, for reasons discussed in the paper, the X-ray was employed to detect the presence of excess solute at the various temperatures which would necessitate the examination of samples in what was considered to be an equilibrium condition. The extremely long annealing periods were used because of the wide discrepancies in the previous investigations, which seemed to be attributable to incomplete equilibrium or possibly the inability to positively identify the precipitate.

## Equilibrium Relations in Aluminum-cobalt Alloys of High Purity

BY WILLIAM L. FINK AND H. R. FRECHE,\* NEW KENSINGTON, PA.

(New York Meeting, February, 1932)

THE constitution of the aluminum-cobalt alloys has been the subject of relatively few investigations. Brunck<sup>1</sup> analyzed the residue which remained after treating the 17 per cent cobalt alloy with dilute hydrochloric acid. The results of the analyses indicated the existence of a compound  $\text{Co}_3\text{Al}_{13}$ . Guillet<sup>2</sup> published a liquidus for the aluminum-cobalt system which contained two maxima corresponding to  $\text{CoAl}_3$  and  $\text{CoAl}_2$  and two eutectic points at 30 and 74 per cent Co. The most extensive investigation of the system was carried out by Gwyer,<sup>3</sup> whose results are summarized in Fig. 1. It will be noted that at the aluminum end there is a suppressed eutectic at  $644^\circ\text{C}$ . By extrapolation of the duration of the eutectic arrest to zero, the composition of the compound was placed at  $\text{Co}_3\text{Al}_{13}$ . Another thermal arrest was noted at  $550^\circ\text{C}$ ., which Gwyer attributed to a peritectic reaction.

The present investigation of the aluminum end of the aluminum-cobalt system is the eleventh of a series dealing with the constitution of aluminum-rich alloys prepared from electrolytically refined aluminum.<sup>4</sup>

*Preparation of Alloys.*—The alloys used in this work were all prepared from electrolytically refined aluminum, the analysis of which is shown in Table 1. In preparing some of the alloys, metallic cobalt (98 to 99 per cent) was used either directly or in the form of an intermediate alloy, the composition of which is given in Table 1. In order to obtain alloys of higher purity, cobalt was introduced into some of the alloys by means of chemically pure cobaltous chloride which was readily reduced by the aluminum. A small electric furnace with nickel-chromium heating elements was used in the preparation of the alloys.

*Chemical Analysis.*—An analysis sample from each melt was chill-cast in the form of a plate  $\frac{3}{16}$  in. thick. In all cases the casting temperature was well above the liquidus. Cobalt was determined electrolytically in all alloys containing more than 0.05 per cent cobalt and by the nitroso-

\* Metallurgical Division, Aluminum Research Laboratories.

<sup>1</sup> *Ber. deutsch. chem. Ges.* (1901) **34**, 2733.

<sup>2</sup> *Etude Théorique des Alliages Métalliques*, 31.

<sup>3</sup> *Ztsch. f. anorg. Chem.* (1908) **57**, 140.

<sup>4</sup> F. C. Frary: Electrolytic Refining of Aluminum. *Trans. Amer. Electrochem. Soc.* (1925) **47**, 275.



and an intermetallic compound. The eutectic composition was approximately 1.45 per cent Co and 98.55 per cent Al with the casting technique employed.<sup>6</sup> As in the case of the aluminum-silicon, aluminum-iron, and aluminum-beryllium systems, the eutectic in chill-cast specimens contains more of the alloying element than does the true (*i. e.*, equilibrium) eutectic. Otherwise the structures were similar to, but finer than, those of specimens which had solidified and slowly cooled in the furnace, shown in Figs. 2 and 4. Both the primary and the eutectic particles of the

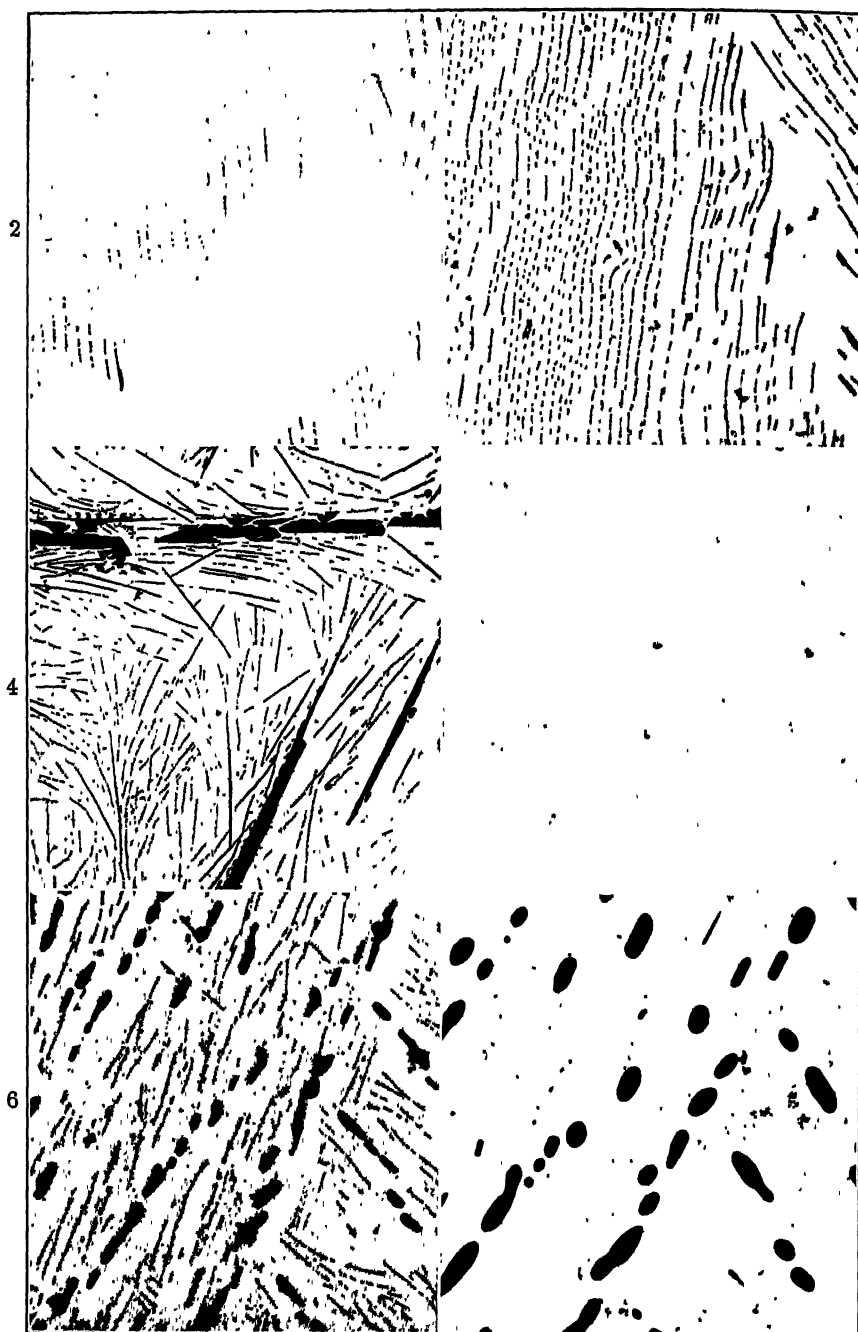
TABLE 1.—*Chemical Composition of Alloys*

Description of Sample	Sample No.	Composition of Alloys, Per Cent				
		Co	Ni	Fe	Si	Cu
Electrolytically refined aluminum				0.008	0.005	0.012
Cobalt-rich alloy prepared from metallic cobalt.... .	963	15 68	0.36	0.13	0.13	0.01
Cobalt-rich alloy prepared from CoCl <sub>2</sub> ..... .	4476	2.61	trace	0.03	0 01	0.01
Prepared from						
sample 4476... .	4276	0.01				
sample 4476..... .	4275	0.02				
sample 4476 ..... .	4274	0.03				
sample 963..... .	1823	0.05				
sample 963..... .	1077	0.32				
sample 963..... .	1079	0.55				
sample 963... .	1083	1 25				
sample 963..... .	1080	1.45				
sample 963..... .	1084	1 69				
sample 963..... .	1085	1 92				
sample 963..... .	1086	2.42				
sample 963..... .	1087	3.22				

intermetallic compound appeared in the section, as needles which exhibited a lavender color in the unetched condition when illuminated by light from a carbon arc filtered through a 78A Wratten filter (*i. e.*, light which closely approximates daylight). The constituent was unaltered by 1 per cent hydrochloric acid, 20 per cent sulfuric acid at 70° C., 1 per cent sulfuric acid, or 1 per cent nitric acid. When etched with a 25 per cent solution of nitric acid at 70° C. for 40 sec. and quenched, the constituent turns bluish gray. A 2 per cent sodium hydroxide solution also colors the particles gray. The particles are colored brown to black by 0.5 per cent solution of hydrofluoric acid, and by a solution

<sup>6</sup> E. H. Dix, Jr. and W. D. Keith: Equilibrium Relations in Aluminum-manganese Alloys of High Purity. *Proc. Inst. Met. Div., A. I. M. E.* (1927) 315.





FIGS. 2-7.—CAPTIONS ON OPPOSITE PAGE.

composed of 1 c.c. hydrofluoric, 1.5 c.c. hydrochloric, 2.5 c.c. nitric acid and 95 c.c. water.<sup>7</sup>

*Composition of the Constituent Occurring in Aluminum-rich Alloys.*—

The composition of the constituent at the aluminum end of the system was determined by dissolving away the aluminum of the furnace-cooled samples containing 15.68 per cent Co (sample 963) and 2.61 per cent Co (sample 4476) and analyzing the large clean crystals, which were selected from the residue under a binocular microscope. The matrix was dissolved both chemically in 2 per cent hydrochloric acid solution, and anodically<sup>8</sup> in a solution of citric acid and sodium chloride buffered with secondary sodium phosphate. The analysis of the crystals recovered from the alloy prepared from cobaltous chloride corresponded to the formula  $\text{Co}_2\text{Al}_9$ . The crystals that were obtained from the alloy prepared from metallic cobalt contained some nickel and iron. If the results are corrected for the impurities on the assumption that iron and nickel atoms replace cobalt atoms in the lattice, the corrected analyses correspond to  $\text{Co}_2\text{Al}_9$  with a maximum error of 0.3 per cent Co. In view of these results, it is believed that the formula  $\text{Co}_2\text{Al}_9$  is more probable than  $\text{Co}_3\text{Al}_{13}$ , which differs from  $\text{Co}_2\text{Al}_9$  by 0.8 per cent Co.

*Thermal Analysis.*—Cooling curves were taken of alloys up to 3.22 per cent Co. A sample of about 200 g. in a graphite crucible was heated in a small electric furnace to a temperature well above the liquidus and cooled at a rate of approximately 5° C. per minute. The temperatures were read by means of a Leeds & Northrup precision potentiometer (type K) and a platinum, platinum-rhodium thermocouple with an iced cold junction. The couple was carefully calibrated against the freezing point of electrolytically refined aluminum (660° C.) and was protected from the melt according to the practice recommended by the U. S. Bureau of Standards.<sup>9</sup>

<sup>7</sup> E. H. Dix, Jr. and F. Keller: *Min. & Met.* (1928) 9, 327.

<sup>8</sup> W. L. Fink and K. R. Van Horn: *Constituents of Aluminum-iron-silicon Alloys. Trans. A. I. M. E., Inst. Met. Div.* (1931) 383.

<sup>9</sup> U. S. Bur. Stds. *Tech. Paper* 170 (1921) 193.

FIG. 2.—0.6 PER CENT COBALT ALLOY (Y1079-A-789).  $\times 500$ .

Specimen cooled through freezing range at approximately 5° C. per minute. Etched with 0.5 per cent HF.

FIG. 3.—1.12 PER CENT COBALT ALLOY (Y1082-A-497).  $\times 500$ .

Specimen cooled through freezing range at approximately 5° C. per minute. Etched with 0.5 per cent HF.

FIG. 4.—1.45 PER CENT COBALT ALLOY (Y1080-A-520).  $\times 500$ .

Specimen cooled through freezing range at approximately 5° C. per minute. Etched with 0.5 per cent HF.

FIG. 5.—0.02 PER CENT COBALT ALLOY (Y4275-A-1031).  $\times 500$ .

Specimen heated 48 hr. at 630° C. Unetched. Shows small particles of  $\text{Co}_2\text{Al}_9$ .

FIG. 6.—CHILL-CAST 3.22 PER CENT COBALT ALLOY (Y1087-A-14875).  $\times 500$ . Etched with 0.5 per cent HF.

FIG. 7.—SAME AREA AS IN FIG. 6.  $\times 500$ .

Specimen heated four weeks at 630° C. Etched with 0.5 per cent HF.

None of the alloys investigated exhibited more than two thermal arrests. The primary arrests were subject to undercooling, so that they contributed no reliable data. The average of the eutectic temperatures of the samples prepared from metallic cobalt was  $656.5^{\circ}$ , but that obtained from several cooling curves and heating curves of sample 4476 prepared from cobaltous chloride was  $657^{\circ}$  C. The latter is probably more accurate. Contrary to results reported in the literature, no thermal arrest was found at  $550^{\circ}$  C.

*Determination of the Hypereutectic Liquidus.*—Since the primary arrests on the cooling curves of the hypereutectic alloys are weak and subject to undercooling, the hypereutectic liquidus was determined by analyzing the melt in equilibrium with the precipitated crystals of  $\text{Co}_2\text{Al}_9$ . This is the method commonly used to determine the solubility in aqueous systems and has been used in the study of two metallic systems.<sup>10</sup>

A 15-lb. charge of aluminum-cobalt alloy containing 10 per cent Co was heated in a plumbago crucible to  $990^{\circ}$  C., cooled to  $877^{\circ}$  C. and maintained at that temperature for 2 hr. After removing the dross from the surface of the melt, a sample for chemical analysis was taken with a ladle preheated to the temperature of the melt. The sample was chill-cast in the form of a  $\frac{3}{16}$ -in. thick slab. The temperature was slowly decreased to  $830^{\circ}$  C., held at that temperature, and an analysis sample taken as before. This gradual dropping of the temperature, holding at temperature, and taking of samples was continued to  $675^{\circ}$  C. Table 2 gives the results of two such experiments.

TABLE 2.—*Solubility of  $\text{Co}_2\text{Al}_9$  in Molten Aluminum*

First Experiment		Second Experiment	
Temperature, Deg. C.	Cobalt, Per Cent	Temperature, Deg. C.	Cobalt, Per Cent
877	8.28	768	3.18
875	7.68	766	3.19
832	5.53	748	2.72
780	3.64	748	2.73
734	2.40	735	2.41
700	1.44	733	2.34
675	1.24	728	2.17
675	1.18	728	2.12
		709	1.82
		709	1.83
		695	1.70
		680	1.40

<sup>10</sup> H. J. Miller: The Penetration of Brass by Tin and Solder with a Few Notes on Copper-Tin Equilibrium Diagram. *Jnl. Inst. Metals* (1927) **37**, 188.

W. L. Fink, K. R. Van Horn and P. M. Budge: Constitution of High-purity Aluminum-titanium Alloys. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 421.

*Eutectic Composition.*—The intersection of the hypereutectic liquidus (extrapolated by means of an empirical formula) with the eutectic horizontal places the eutectic composition at 1.0 per cent Co and 99 per cent Al. This eutectic composition was approximately verified by microscopic observation of specimens solidified and slowly cooled in the furnace. A specimen containing 1.12 per cent Co consisted largely of eutectic areas such as that shown in Fig. 3. Some small particles of  $\text{Co}_2\text{Al}_9$  may be primary. No segregation of primary  $\text{Co}_2\text{Al}_9$  was found at the bottom of this specimen. All specimens of higher cobalt content

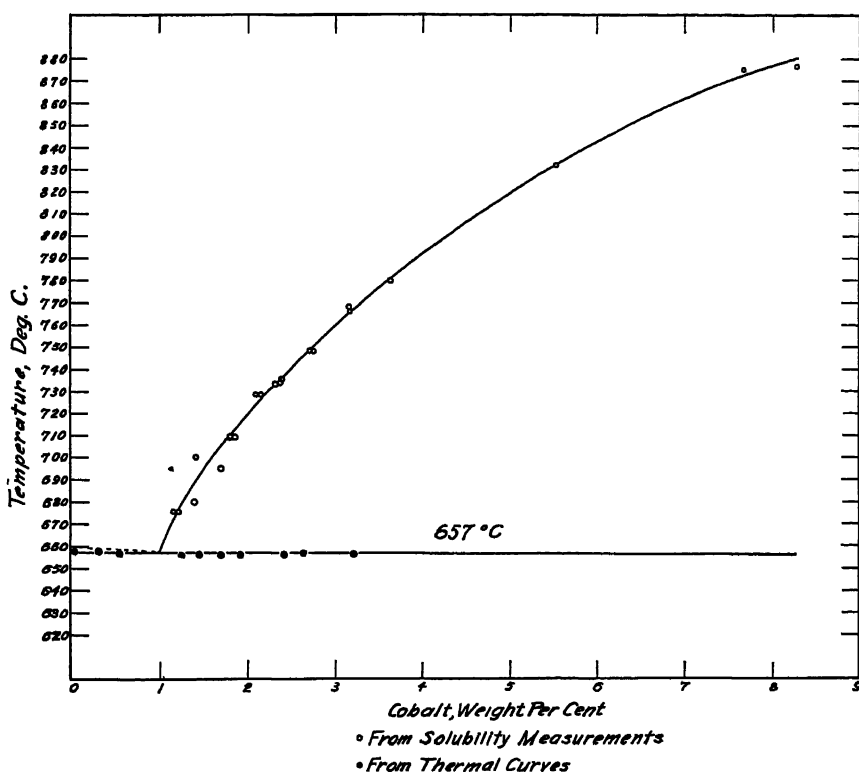


FIG. 8.—ALUMINUM END OF ALUMINUM-COBALT DIAGRAM.

contained large particles of  $\text{Co}_2\text{Al}_9$  (similar to those shown in Fig. 4) which had settled to the bottom during solidification. Throughout the specimens containing 0.9 per cent Co and less, there were primary aluminum dendrites, as shown in Fig. 2.

*Solid Solubility of Cobalt in Aluminum.*—Examination of a series of chill-cast specimens (prepared from metallic cobalt) heated for four weeks at 630° C. and quenched indicated that the solubility was less than 0.05 per cent Co at that temperature. A second series of alloys (0.01,

0.02, 0.03 per cent Co, samples 4274 to 4276) was chill-cast in the form of 1-lb. ingots, and cold-rolled to 22-gage sheet. Samples of this sheet were heated at both 630° C. and 655° C. for 48 hr. and quenched. The solubility at both temperatures was less than 0.02 per cent Co. Fig. 5 shows particles of  $\text{Co}_2\text{Al}_3$  out of solution in the 0.02 per cent cobalt sample which had been heated at 630° C. No particles of  $\text{Co}_2\text{Al}_3$  could be found in the 0.01 per cent Co specimen.

The solid solubility, however, is sufficient to allow spheroidization. For example, Figs. 6 and 7 show the same area of a chill-cast 3.22 per cent Co alloy before and after annealing for four weeks at 630° C.

*Aluminum End of Aluminum-cobalt Diagram.*—The aluminum-cobalt diagram from 0 to 8 per cent Co is represented in Fig. 8. The hypereutectic liquidus and the eutectic have been determined experimentally, as described. The hypoeutectic liquidus is represented by a straight dotted line drawn from the freezing point of pure aluminum to the eutectic point. The solid solubility of cobalt in aluminum is less than 0.02 per cent at 655° C., and therefore could not be indicated on the diagram.

## DISCUSSION

(*W. M. Peirce presiding*)

MEMBER.—Is solid solubility necessary for spheroidization, or is it not possible that a force of surface tension would account for that?

W. L. FINK.—Perhaps spheroidization was not the term that I should have used. The particles were not only spheroidized but larger, and the small eutectic needles had completely disappeared. That is what I had in mind rather than the spheroidization of a particle without any change in size.

W. M. PEIRCE, Palmerton, Pa.—I would like to ask about one possible source of error in this method of determining the composition of a melt in equilibrium with a constituent which is freezing out. Might not some convection currents exist which would keep some of the frozen crystals in suspension and result in their being taken with the sample of melt? Of course, there is the advantage of a relatively large difference in density when dealing with an alloy of aluminum and a heavier metal, but in spite of that is there not a possibility of error?

W. L. FINK.—That source of error was considered. As a matter of fact, there are other sources of error which are more serious. Plates of constituent grow out from the sides of the crucible and from the dross film on the surface of the melt, and it is necessary to skim the melt thoroughly several times before taking a sample. We believe, however, that the results approach very closely true equilibrium when the samples are taken with care. The particles of constituents, under the conditions of the experiment, grow to a fairly large size and being much more dense than the metal they sink readily to the bottom unless they are attached to the crucible or to dross, as mentioned above.

If some of these particles were carried by convection currents we would find, upon analysis, that we had too much of the alloying element present. As a matter of fact, we never get conditions that give more of the alloying element than is revealed by thermal analysis. The difference is usually in the opposite direction. That is, either we settle out more material than would be indicated by thermal analysis (the thermal analysis being an error on account of undercooling) or else the two methods agree.

## Preparation of Graded Abrasives for Metallographic Polishing

By J. L. RODDA,\* PALMERTON, PA.

(Boston Meeting, September, 1931)

THE desirability of a uniformly sized abrasive for metallographic polishing has probably been recognized in a general way for a long time. Certainly all metallographers have recognized the damage that can be done to a polished surface by a piece of grit, especially if one of the softer metals, such as zinc or aluminum, is being polished. It is to be doubted, however, whether many metallographers have had any adequate idea of the particle size of the abrasives they were using or of the range of sizes encountered in any given grade of abrasive. At any rate, the descriptions of abrasives for metallographic work found in the literature are generally very meager.

It was with the idea of securing an abrasive with a limited range of particle size that a study of this problem was commenced.

Commercial abrasives, even when recommended for metallographic work, are made up of particles of varying sizes. One such abrasive contains some particles so fine that they remain in suspension for days and other particles so coarse that they settle at the rate of 3 in. per minute. It is evident that the coarsest particles are over 100 times the diameter of the smallest ones, or over 1,000,000 times the volume. The hopelessness of avoiding scratches under these conditions is evident.

Vanderwilt<sup>1</sup> has described a laboratory method for grading abrasives in which the elutriator is used. Le Chatelier's method, described by Goerens,<sup>2</sup> also makes use of an elutriator. However, the elutriator is too slow for this purpose and requires too delicate a control for the range of sizes desired. The method of stirring up the abrasive in water, allowing it to settle for a given time, then drawing a measured depth off the top of the suspension, has been finally adopted as the simplest procedure. The largest particle in a given portion is then determined by Stokes' law:<sup>3</sup>

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\* Investigator, Metal Section, Research Division, New Jersey Zinc Co.

<sup>1</sup> J. W. Vanderwilt: A Laboratory Method for Grading Abrasives. *Econ. Geol.* (1929) 24, 853-859.

<sup>2</sup> P. Goerens: Introduction to Metallography. Translation by Ibbotson. London, New York, Bombay and Calcutta, 1908. Longmans, Green and Co.

<sup>3</sup> J. H. Calbeck and H. R. Harner: Particle Size and Distribution by Sedimentation Method. *Ind. & Eng. Chem.* (1927) 19, 58-61.

$$r^2 = \frac{9}{2} \frac{nh}{(d_1 - d_2)60gt} \quad [1]$$

when

- $r$  = radius of spherical particle,  
 $n$  = viscosity of medium,  
 $h$  = distance of sedimentation, centimeters,  
 $d_1$  = specific gravity of dispersed phase,  
 $d_2$  = specific gravity of dispersing medium,  
 $g$  = acceleration due to gravity, centimeters per second, per second,  
 $t$  = time, minutes.

With the selection of a given abrasive such as alumina all quantities except  $r$ ,  $h$  and  $t$  become constants. We may then write the equation as follows:

$$r^2 = \frac{h}{kt} \quad [2]$$

Merely by fixing  $h$  and  $t$  an abrasive may be obtained whose particle size is a constant.

#### EXPERIMENTAL PREPARATION OF ABRASIVE

Stokes' law, of course, is based on the assumption that each particle is free to fall by itself; that there is no flocculation or attachment of any particle to its neighbor. This condition is not realized ordinarily when an abrasive is stirred up with water. In such a suspension a flocculate of 10 small particles will settle at the same rate as a much larger single particle.

The first requirement, then, is that the abrasive be thoroughly dispersed in the water. The method which has been adopted in this laboratory is to put the abrasive and water through a colloid mill with a small amount of sodium silicate as a dispersing or peptizing agent. Running the suspension in a pebble mill for 2 hr. will accomplish the same result.

It was first necessary to decide on some standard for the coarsest and finest abrasives to be obtained. The coarsest abrasive for zinc and zinc alloys should be one that will remove the scratches from the 3/0 emery paper with a reasonably short polish. The finest abrasive should give a polished surface free from scratches. An alumina which settles at the rate of 1 in. in 4 or 5 hr. gives a polished surface free from all but the most minute scratches with a given zinc alloy. An alumina settling at the rate of 3 in. per minute removes the scratches from 3/0 emery paper with a reasonably short polish. With these facts in view, the following four grades of alumina were decided upon:

TIME REQUIRED TO SETTLE ONE INCH	RATIO OF DIAMETERS OF LARGEST PARTICLES
4 hr.	1
30 min.	2.82
3 min.	8.96
20 sec.	26.8

Each grade has approximately three times the diameter of the next finest grade. It should be kept in mind that these sizes were chosen for zinc and its alloys. Each metallographer must decide for himself the range of sizes best suited to his work, since the metals vary greatly in hardness and susceptibility to scratching.

In the preliminary work, dealing with a slightly different range of settling times, the fractions siphoned off were frequently checked with the microscope for particle size. Each fraction was found to cover a uniform range. The uniformity of the particles of maximum size was particularly noteworthy. This microscopic examination also showed that the particles were not flocculated, but that each one settled separately.

When the abrasive is thoroughly dispersed it settles to the bottom of the beaker in a hard, compact cake, much like the cake formed by clay upon settling. This is especially true of the fine sizes. It is an indication of good dispersion. Once the cake is formed it is a difficult task to stir it up again, but when stirred up the abrasive is again thoroughly dispersed.

It is advisable, therefore, to keep the abrasive intended for immediate use on the wheels stirred at all times. The container illustrated in Fig. 1 does this in a very satisfactory manner. When it is desired to use the abrasive on the polishing wheel, the screw clamp is tightened up and the tube *c* disconnected at *a*. Abrasive is then allowed to drip on the wheel from the end of *c*. It is advisable to have an additional screw clamp at *b* to regulate the amount of abrasive dripping on the wheel.

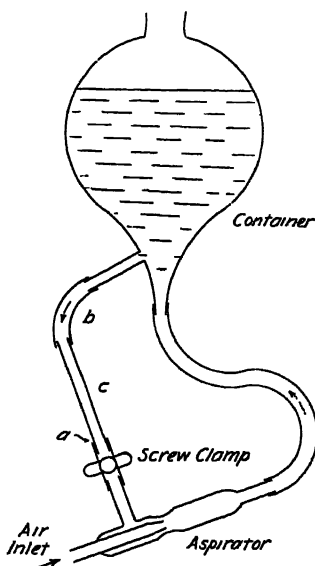


FIG. 1.—CONTAINER AND STIRRER FOR ABRASIVE SUSPENSIONS.

#### RECOMMENDED PROCEDURE

In the following description of the method used in preparing the four grades of abrasive, the grades are taken up in the order of their separation from the raw alumina rather than in the order of their use on the wheels.

##### *Abrasive for Fourth Wheel*

To each 100 g. alumina add 1 c.c. of 40 per cent sodium silicate and approximately  $\frac{1}{2}$  liter of water. Run through a colloid mill about three times or grind 2 hr. in a pebble mill. Stir up the suspension and allow it



to stand 4 hr. Siphon off the top inch, being careful not to allow the tip of the siphon to extend more than 1 in. below the surface. After another 4 hr. again siphon off the top inch. Repeat this process until the level of the suspension is almost down to the settled cake in the bottom of the beaker. (If desired the beaker may stand 8 hr. and the top 2 in. be siphoned off, etc.). Stir up the cake in the bottom of the beaker with fresh water and after it has stood for 4 hr. again siphon off the top inch. (A spatula is useful in cutting the settled cake loose from the bottom of the beaker.) When the suspension siphoned off is too thin for use, the abrasive is ready for the separation of the next fraction.

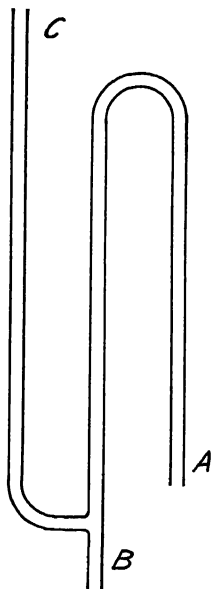


FIG. 2.—SIPHON.

#### *Abrasive for Third Wheel*

Stir up the cake in the bottom of the beaker with water and allow it to stand  $\frac{1}{2}$  hr. Siphon off the top inch. This process is repeated as in the previous case until the suspension siphoned off is too thin for practical use.

#### *Abrasive for Second Wheel*

Stir up the residue from the last separation with water. After 3 min. siphon or pour off the top inch of solution. Since the siphoning should be done at a slow enough rate so that abrasive is not drawn up from the lower layers of suspension, the siphoning itself may take sufficient time to alter the size of the abrasive drawn off. By selecting a beaker<sup>4</sup> and siphon of the proper size, 2 in. of suspension may be drawn off in 3 min. Then

the procedure is to allow the suspension to stand 3 min. after stirring, then occupy another 3 min. in drawing off 2 in. of suspension, taking care not to insert the tip of the siphon too deeply into the suspension.

#### *Abrasive for First Wheel*

Stir up the residue as before and allow it to stand 20 sec. Pour off the top inch of suspension. Repeat until there is not sufficient residue for further separation.

The form of siphon shown in Fig. 2 is recommended to those not already familiar with it. The limb A is placed in the liquid to be siphoned. The mouth is placed at C and suction applied while the end of B is covered with the finger. When once started the finger and mouth are removed and the siphon functions normally.

<sup>4</sup> The settling cylinder should be a 2-liter beaker, 5-in. diameter.

## GRADES AND APPLICATIONS OF ABRASIVES

Photomicrographs of the four grades of abrasive separated by the foregoing method are shown in Figs. 3 to 6, inclusive. The data in the captions indicate the approximate volume of the largest particles as calculated from a diameter of one of the largest particles shown. As we had a considerable stock of emery on hand when this work was started we have been using the emery with the alumina. Emery is chiefly corundum, chemically the same as alumina. The chief impurity is magnetite, which has a specific gravity of 5.18 as against 4.0 for corundum. Equation 2 then does not strictly hold and, as will be seen from the photomicrographs, there is a tendency for the heavier magnetite to concentrate in the coarser portions. The discrepancy probably is not serious, however, and at least lies in the right direction, since the foreign particles are smaller than the corundum and therefore will not cause deep scratches. The dispersion of the emery seems to take place with less frothing if a portion of alumina is added to it before it is put through the colloid mill. The alumina has given no trouble with frothing. All four grades of abrasive have been obtained from the same alumina, selling at about 40¢ per pound.

For most polishing where the specimen is to be etched afterward, it is sufficient to polish on the first three wheels only. Where a soft metal is to be photographed in the unetched condition, or where one constituent remains unetched, it is necessary to polish on the fourth wheel to obtain a good looking specimen.

There is a tendency for the abrasive to embed itself in the surface of the zinc, especially on the third and fourth wheels. This is due primarily to the soft surface of zinc, but probably the type of cloth used on the wheels and the amount of pressure applied are also important factors.

Ground zinc oxide ("rock oxide") has been used successfully for polishing after separation in this manner, so the method should be of general application.

A number of photomicrographs are shown to illustrate the results obtained with the selected abrasives.

Figs. 7 and 8 show a zinc-base die-casting alloy to which silicon was added for experimental purposes. The crystals probably are elemental silicon. The manner in which the fine details of the crystals are preserved is noteworthy. The crystals are slate blue in color<sup>5</sup> and are much more readily detected in an unetched section than in the etched specimen. Figs. 9 to 11, inclusive, show various types of electroplate on zinc-base alloys. Figs. 7 to 11, inclusive, are all unetched. Etching of a plated

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<sup>5</sup> E. H. Dix, Jr. and A. C. Heath, Jr.: Equilibrium Relations in Aluminum-silicon and Aluminum-iron-silicon Alloys of High Purity. *Proc. Inst. Met. Div., A. I. M. E.* (1928) 164-197.



FIGS. 3-14.—CAPTIONS ON OPPOSITE PAGE.

zinc alloy usually results in deeply etching the zinc and leaving the coating untouched.

The type of specimen in which one constituent remains untouched by the etching reagent shows up to advantage when polished with this abrasive. The white patches of copper-rich  $\epsilon$  in Fig. 14 are unattacked by the etching reagent, while the matrix is etched. Figs. 12 and 13 show a comparison of the results obtained by the old and the new abrasives. The  $\text{FeZn}_7$  crystals have not been attacked by the etching reagent. The etching reagent consists of a solution of 20 g. of C.P. chromic acid in 100 c. c. water to which 0.75 g.  $\text{Na}_2\text{SO}_4$  has been added for Fig. 14 and 1.5 g.  $\text{Na}_2\text{SO}_4$  for Figs. 12 and 13.

### SUMMARY

A method for producing uniformly sized abrasives for metallographic polishing has been described. The essential steps in the process are:

1. Thorough dispersion of the abrasive in water. This is accomplished by using a small amount of sodium silicate as a peptizing agent and dispersing in either a colloid mill or a pebble mill.
2. The abrasive suspension is allowed to settle for a definite time and siphoned off to a predetermined depth, using the siphoned material.

### ACKNOWLEDGMENTS

The photomicrographs of abrasives (Figs. 3 to 6, inclusive) were taken by Mr. Clyde Hall of this laboratory. The suggestions of a number of others from the laboratory have been helpful in carrying out this work.

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- A = FIGS. 3-5. B = FIGS. 6-8. C = FIGS. 9-11. D = FIGS. 12-14.
- FIG. 3.—ABRASIVE FOR FIRST WHEEL—1 IN. IN 20 SEC.  $\times 500$ . MAXIMUM PARTICLE SIZE:  $14,138 \times 10^{-9}$  CU. MM.
- FIG. 4.—ABRASIVE FOR SECOND WHEEL—1 IN. IN 3 MIN.  $\times 500$ . MAXIMUM PARTICLE SIZE:  $524 \times 10^{-9}$  CU. MM.
- FIG. 5.—ABRASIVE FOR THIRD WHEEL—1 IN. IN 30 MIN.  $\times 500$ . MAXIMUM PARTICLE SIZE:  $33.5 \times 10^{-9}$  CU. MM.
- FIG. 6.—ABRASIVE FOR FOURTH WHEEL—1 IN. IN 4 HR.  $\times 500$ . MAXIMUM PARTICLE SIZE:  $1.77 \times 10^{-9}$  CU. MM.
- FIG. 7.—ZINC-BASE DIE-CASTING ALLOY PLUS 0.23 PER CENT SILICON. UNETCHED.  $\times 500$ .
- FIG. 8.—SAME AS FIG. 7.
- FIG. 9.—NICKEL-BRASS PLATE OVER ZINC-BASE DIE CASTING. UNETCHED.  $\times 1000$ .
- FIG. 10.—NICKEL PLATE OVER ZINC-BASE DIE CASTING. UNETCHED.  $\times 1000$ .
- FIG. 11.—NICKEL-CHROMIUM PLATE ON ZINC-BASE DIE-CAST RADIATOR CAP. UNETCHED.  $\times 1000$ .
- FIG. 12.—CASTING OF ZINC + 1 PER CENT IRON. POLISHED BY OLD METHOD. ETCHED.  $\times 100$ .
- FIG. 13.—SAME AS FIG. 12 POLISHED WITH NEW ABRASIVE. ETCHED.  $\times 100$ .
- FIG. 14.—CASTING OF ZINC + 8 PER CENT COPPER. ETCHED.  $\times 100$ .

## DISCUSSION

(Norman B. Pilling presiding)

H. E. WHITE, Zelienople, Pa. (written discussion).—There are a large number of abrasives at present commercially obtainable; emery appears to be the most uniform for polishing purposes such as described. This is probably due to its natural formation. It seems to have less tendency to scratch and can be more easily graded. Anyone interested in this work will enjoy reading two rather ancient articles on the subject. In the *American Journal of Science* in the year 1850 (10, 362) and in the year 1866 (42, 124), J. Lawrence Smith reported some work on determining the effect of hardness of emery and corundum in comparing them to sapphire of India and also to ruby. It is very interesting, in the light of present knowledge, to read these two articles.

Natural corundum appears to be next to emery as far as metallographic polishing characteristics are concerned. It would appear that artificial abrasives such as crystalline alumina would supplant these natural minerals. There are some very carefully prepared materials that do, the reasons being as follows: Emery when crushed seems to break into isometric fragments, artificially prepared crystalline alumina does not. Indiscriminate crushing will produce what are known as flats and slivers similar to those shown in Fig. 3, and these, while they may have the same settling characteristics as the rest of the particles, will not polish to the same degree, and when they are turned on edge will scratch, of course. If the crystalline alumina is crushed in such a way as to produce isometric fragments of coherent structure these flats and slivers will naturally disappear as well as those particles having lines of weakness and any loosely bound agglomerates. The individual grains prepared in this manner will be of uniform strength.

Crystalline alumina has a tendency toward conchoidal fracture and the crushing must be so done as to break up the mass as nearly along the crystalline planes as possible. The intercrystalline glass present will then appear near the outside of the grain. Nearly all crystalline alumina contains magnetic particles, which must be completely removed for careful polishing work.

The author speaks of a frothing when emery is used, I would like to refer him to the articles by Dr. F. J. Preston,<sup>6</sup> which might be of some corollary assistance.

L. L. WYMAN, Schenectady, N. Y.—The author is to be commended for preparing a method that is more simple than the elutriator, although I have some doubt that the ultimate result would be better than could be obtained by an elutriator when it is properly operated. On several occasions I have used the ordinary alumina, which is purchasable at fairly reasonable rates, and prepared it by elutriating, obtaining an extremely good polishing medium for soft materials. It is not necessary to precede this by ball milling or other procedure. It can be taken as received from the chemical supply house and used directly in the elutriator, with a sufficient flow of liquid through the elutriator. Ordinarily there is enough disturbance there to cause the separation of the particles.

The author makes one point which I think is somewhat contrary to the usual conception of the action of powdered materials. On page 151 he says that the settling in a compact cake might be taken as an indication of the fineness of the powder. I think that is quite contrary to the usual operation; a number of years of experience with powdered materials have shown conclusively that with a given medium the materials

<sup>6</sup> F. J. Preston: Chemical and Physico-Chemical Reactions in Grinding and Polishing of Glass. *Jnl. Soc. of Glass Technology* (1930) 14 (54), 127-33.

Abrasives for Glass. *Glass Industry* (1930) 11 (4), 78-79.

that will settle most compactly, or which under any sort of pressure will go down to the most compact size, are those that show a great distribution of particle sizes.

E. M. WISE, Bayonne, N. J.—Since reading Mr. Rodda's paper, we have adopted his procedure and, on the whole, have secured excellent results. An observation was made, paralleling Mr. Wyman's suggestion, that if rather sharply graded fractions were obtained the cake does not settle solidly, and that is one important advantage of the sharply graded abrasive. Sharply graded abrasives cut rapidly without leaving deep scratches—a most valuable characteristic. On the whole, the method seems to work extremely well, and certainly will be appreciated by metallographers who have not been able to obtain from commercial sources material of comparable merit.

L. L. WYMAN.—I should like to make one more statement about the action of these powdered materials. It is the general rule that the finer a powder is (we call it a light powder) the less it settles down. A heavy powder will naturally settle much more than a light powder. However, it is the mixture of the two, the great dispersion, that gives the maximum settling. As an indication of the lightness and uniform lightness of a metal powder, the lack of settling is usually the best indication, short of microscopic determination or something of that nature.

W. M. PEIRCE, Palmerton, Pa.—This method of classifying abrasives is partly the outcome of our experience in the New Jersey Zinc Co. with paint pigments, and our knowledge of what controls dispersion and settling. I do not believe that it is correct to say that fineness determines the compactness of the cake into which a powder will settle. That is determined, as I understand it, quite as much by the relation between particles and the vehicle in which they are suspended.

While I do not know much about pigments, I do know that a pigment of a definite particle size may settle into a very hard cake in one vehicle and not in another. There are a great many factors that enter in, such as the possibility of surface charges on the particles, possibility of adsorbed materials on the particles, and similar factors.

I really believe that the most important element in this new method is the use of a dispersing agent to insure separate and distinct particles in suspension before starting to classify them.

J. L. RODDA.—I am particularly glad to hear the remark on the difference between artificial and natural abrasives, the difference in the cleavage. That is a factor, of course, with which we were not dealing here, but it is an interesting factor which is to be considered as far as the efficiency of the abrasive is concerned.

I cannot entirely agree with Mr. Wyman that we can procure thorough dispersion of the abrasive without the use of a dispersing agent. Alumina seems to disperse to some extent without the addition of sodium silicate, but not all of it. A portion of it is not thoroughly mixed with the water. Emery is even more troublesome in that respect and without the addition of the dispersing agent it is almost impossible to proceed with this method. Aggregates, too, I believe are generally so closely attached that the action of a stream in an elutriator would not be sufficient to break them up. That stream would have to be too slow for the size of abrasives with which we are dealing here.

It may be true that if the abrasive is more closely sized than ours were the abrasive may settle to a looser cake. Of course we allowed in this classification for a variation of 1 to 3 in the diameter of particles within any given grade. If desired it would be very easy to make a closer grading.

There might be a dozen different grades if desired, but that would necessitate a dozen polishing wheels in the process, and I think the time in transferring the specimen from one wheel to the next would destroy any value from the use of such closely graded abrasives.

J. L. RODDA (written discussion).—Additional work since presentation of the paper may throw some light on Mr. Wyman's experience in dispersing alumina. We have found that all grades of artificial alumina do not behave alike. One grade may be dispersed without the use of sodium silicate and a colloid mill or pebble mill, while another grade requires this treatment for thorough dispersion. It is, of course, possible that some dispersing agent is at times introduced in the course of manufacture.

## The Beta to Alpha Transformation in Hot-forged Brass

BY ROBERT S. BAKER,\* WATERBURY, CONN.

(Boston Meeting, September, 1931)

It has been demonstrated in the laboratory by A. J. Phillips<sup>1</sup> that a transformation or conversion from beta directly to alpha may take place in a brass of 61 to 62.5 per cent copper content. The completion of the transformation is dependent on a rapid rate of cooling from the all-beta field through the alpha + beta range to the alpha field. Phillips states that in a slowly cooled alloy containing 62 per cent copper and 38 per cent zinc the copper content of the beta is progressively decreased from 62 to 56 per cent by precipitation of alpha. Rapid cooling tends to prevent the separation of alpha with a copper content of more than 62 per cent by reducing to a minimum the time required for passing through the alpha + beta range. Upon crossing beyond the (alpha + beta) (alpha) boundary to the all-alpha region below, the material is transformed from beta to alpha. It is essential that there be no change in composition. Phillips obtained his results by quenching a 62:38 copper-zinc alloy from 850° C. in iced brine at -8° C.

No reference to the occurrence of this transformation in a manufacturing process has been found in the literature. An investigation of the microstructures of a number of hot forgings made from leaded brass rods yielded one forging in which this striking conversion from beta to alpha had occurred. The purpose of this paper is to describe the transformation and certain conditions under which it may occur during the hot pressing of brass.

The conversion was noted in a shape forged from a leaded brass rod, the composition of which was: Cu, 60.26 per cent; Zn, 37.86; Pb, 1.88. In this study the lead content was disregarded and the alloy was considered to be equivalent to an alloy of 61.40 per cent copper and 38.60 per cent zinc (9812 parts = 100 parts). The possibility that the lead might obstruct or accelerate the precipitation of alpha was not studied. The lead appears as black globules in the photomicrographs and has a negligible solubility in the alloy.

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\* Research Laboratory, The American Brass Co.

<sup>1</sup> A. J. Phillips: The Alpha-beta Transformation in Brass. *Trans. A. I. M. E., Inst. Met. Div.* (1930) 196.



Fig. 1 shows a plan and elevation of a section of the forging. The shaded areas indicate the position of those portions converted to large-grained masses of alpha, each surrounded by an alpha + beta fringe or field. Usually a mottled structure made up of an intimate mixture of alpha and beta (Fig. 2) results from hot-forging a rod into this shape. Fig. 3 shows transformed alpha very similar to that shown by Phillips. Fig. 4 portrays the boundary line between the alpha + beta and the transformed alpha. The locations of the fields shown in the photomicrographs are indicated in the diagram (Fig. 1.)

The transformed alpha was not darkened by the ferric chloride etching reagent customarily used for darkening beta. The characteristic alpha twins were seen.

Phillips' experiment was repeated, as a further check, with samples cut from the original forging. These were annealed at 850° C. for  $\frac{1}{2}$  hr. and quenched in brine at temperatures between -10° and -17° C. The beta to alpha transformation occurred as shown in Fig. 5.

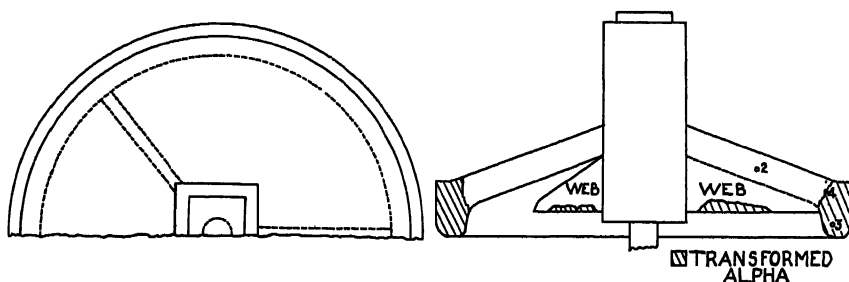


FIG. 1.—PLAN AND ELEVATION OF SECTION OF HOT FORGING IN WHICH BETA TO ALPHA TRANSFORMATION OCCURRED.

Approximately  $\frac{3}{4}$  actual size. Locations of fields shown in Figs. 2, 3 and 4 are indicated.

In order to be sure the forging was not low in zinc in the alpha fields, a specimen containing transformed alpha was annealed and quenched from the alpha-beta range. A uniform Muntz metal structure resulted. The all-alpha field should have been retained if the alpha grains were due to a lower zinc content.

The physical conditions necessary for the conversion, as stated by Phillips, doubtless were met in the forging in which the transformation occurred; *i.e.*,

1. The copper content must be between 61 and 62.5 per cent.
2. The alloy must be heated into the all-beta range.
3. The cooling rate must be rapid enough to prevent any change in composition.

The usual practice in forging a brass of this composition is to heat the slugs to between 700° and 750° C. and then forge on a die preheated above



FIG. 2.—ALPHA + BETA (INCLUDING A LEAD PARTICLE).  $\times 500$ . ETCHED IN  $\text{FeCl}_3$ .

Usual structure obtained when forging this shape.

FIG. 3.—TRANSFORMED ALPHA, FRINGE OF ALPHA + BETA, AND LEAD PARTICLES.  $\times 75$ . ETCHED IN  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ .

FIG. 4.—CONTRASTING STRUCTURE. FINE ALPHA + BETA (ABOVE) AND TRANSFORMED ALPHA (BELOW).  $\times 500$ . ETCHED IN  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ .

FIG. 5.—SPECIMEN CUT FROM FORGING, ANNEALED  $\frac{1}{2}$  HR. AT  $850^\circ \text{C}$ , THEN QUENCHED QUICKLY TO  $-17^\circ \text{C}$ .  $\times 75$ . ETCHED IN  $\text{NH}_4\text{OH} + \text{H}_2\text{O}_2$ .

Entire field is transformed alpha (with lead particles).

200° C. Forgings of a type similar to that referred to above were carefully made in this manner. The transformation did not occur in these samples, although by microscopic examination a considerable heat gradient across the forgings was noticed. The temperature was then raised to 850° C. and several slugs were forged. The die was not especially cooled. A small field of transformed alpha was noted along the die side of one sample of the composition: Cu, 60.27 per cent; Zn, 37.89; Pb, 1.74.

Undoubtedly steel as a quenching medium has one advantage which helps to counterbalance the effect of the lower temperature obtainable with the brine. There is no steam jacket formed when the steel comes in contact with the forging. The formation, momentarily, of such a jacket in a brine bath prevents the instantaneous wetting of the surface of the specimen. The contact between the die and the forging is continually improved by the forging operation, which gives immediate close contact and aids the interchange of heat. It will be recalled that the transformed alpha was found next to the die in both the original specimen and in the mill specimen forged from 850° C.

#### SUMMARY

1. The transformation occurred in all cases in a forging from a rod containing approximately 60.3 per cent copper and 1.75 per cent lead.
2. The rod was heated above 800° C. before forging.
3. The die does not have to be cold to cause the transformation, although a cold die would undoubtedly be more effective.

The transformation from beta to alpha is a matter of academic interest until it appears in a manufactured article. The rim of the original forging in which the transformation was noted was imperfectly formed. The flow of the metal into the die had been arrested and the presence of the transformed alpha gave a clue as to what had occurred. Corrective measures were devised and applied, resulting in perfect forgings.

#### ACKNOWLEDGMENT

The author wishes to acknowledge his indebtedness to Mr. C. H. Davis for his helpful suggestions and criticisms in the preparation of this paper, and to thank The American Brass Co. and Mr. W. H. Bassett for permission to publish these observations.

#### DISCUSSION

R. F. MEHL, Middletown, Ohio (written discussion).—It is always gratifying to a scientific man to find some occasion where scientific knowledge derived for its own sake may be used practically, and such an instance we have here in Mr. Baker's extension of Dr. Phillips' earlier work into practice—even though here, as so frequently, the thing interesting scientifically is to be avoided!

The type of change shown in these alloys is of great interest. It is a type of change—a “suppressed constitutional change” to use Sachs’ term—very similar to that operating in the austenite-ferrite change in quenched Fe-C alloys, for in both cases a phase entirely stable at a high temperature transforms bodily to one stable at a low temperature. It may be suspected immediately that such changes proceed according to some crystal geometry, that the type of structure obtained should be of the nature of a Widmanstätten figure. This crystallographic relationship in hyper-eutectoid Fe-C alloys has been completely analyzed by Kurdymov and Sachs,<sup>2</sup> and found to be explicable in simple lattice geometry.

Such a relationship probably results also in the  $\beta - \alpha$  transformation in Cu-Zn alloys described by Dr. Phillips and Mr. Baker. Indeed, an inspection of Mr. Baker’s Fig. 5 supports such a belief, for the action of the etching agent has brought out two or three groups of  $\alpha$  areas distinguishable by their efficiency in the reflection of light. There is a white group, a gray group, and a nearly black group within one original  $\beta$  grain. It is easy to believe, therefore, that one  $\beta$  grain forms a few orientations of  $\alpha$ , not an infinite number, and that this uniqueness originates in a crystallographic mechanism operating during transition.

The X-ray technique used by Kurdymov and Sachs, or even a simpler technique, should be applicable here in the determination of the orientation of the  $\alpha$  areas; the ease with which large grains of the  $\beta$  phase may be grown would facilitate the experimentation. A complete solution of the crystallographic problem would require a determination of the orientation of the original  $\beta$  lattice, and this might be awkward, but a solution of the finite number of orientations of the  $\alpha$  phase probably would indicate the original orientation of the lattice. This type of structure might well give a simpler solution than that obtained (incompletely) for slowly cooled alloys, by Mehl and Marzke,<sup>3</sup> and possibly would assist in a completion of their work. Certainly the structure which Dr. Phillips discovered is sufficiently striking to warrant an accurate crystallographic analysis.

A. J. PHILLIPS, Maurer, N. J. (written discussion).—I have made examinations with the idea of determining the type of Widmanstätten structure obtained by the conversion of beta into alpha directly, and find that the structure instead of being simpler than that obtained by slow cooling is considerably more complex. It is very easy to find as many as seven crystal orientations of alpha within a single beta grain, whereas one seldom finds more than four orientations of alpha separating from a slowly cooled beta grain.

I have been rather surprised to find that the practical significance of the basic principles governing the phenomenon described by Mr. Baker has not been generally recognized.

In certain hot forging operations where very thin wall sections are produced, it has been found that the entire wall will apparently be all alpha if the composition is about 61 to 62 per cent copper and the extrusion temperature above 825° C. However, hardness tests on these sections yielded values considerably higher than would be expected from an all-alpha structure, and seem to indicate that there are at least submicroscopic particles of beta present, hardening the structure. A short anneal lowered the hardness value to that normal for pure alpha structure. In this connec-

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<sup>2</sup> G. Kurdymov and G. Sachs: The Mechanism of the Hardening of Steel. *Zisch. f. Phys.* (1930) 64, 325.

<sup>3</sup> R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structure, II.—The  $\beta$  Copper-zinc and the  $\beta$  Copper-aluminum Alloys. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 123.

tion it would be interesting to know the hardness values of the forging described by Mr. Baker.

In forging ordinary brass objects the wall sections as a general rule are too heavy for very rapid cooling, so that it is difficult, if not impossible, to directly convert beta into alpha. However, by forging above 825° C. the cooling action of the dies is generally rapid enough to prevent any considerable separation of alpha in the upper temperature range, so that the forgings eventually consist of a very intimate mixture of alpha plus beta, which upon subsequent annealing may be readily converted into alpha.

When a stiff forging is desired, the all-alpha structure should be avoided. However, when forgings are to be cold-pressed or reworked to their final shape a ductile all-alpha structure will make these operations much easier.

In the extrusion process for producing rods, tubes and shapes, it seems to be generally considered that cold extrusion and slow cooling will produce the most ductile products with a minimum of beta. This is true only if the products are to be drawn as extruded. If an anneal is used immediately after extrusion, it will be found that products extruded hot, above 825° C., and rapidly cooled will be more ductile than those extruded cold. In fact, cold extrusion will result in the formation of beta stable enough to persist through several commercial anneals, whereas the beta produced by hot extrusion can often be assimilated in one anneal. It is assumed that the annealing temperature will be low enough to be within the all-alpha field. Annealing in the alpha-beta field will merely stabilize the beta constituent, of course.

R. S. BAKER (written discussion).—The practical value of the transformation has been outlined by Dr. Phillips. A word of caution should be added; his remarks deal with nonlead stock and a great many hot forgings are made from lead stock. A temperature of 800° to 850° C. introduces difficulties in hot-working lead stock.

The use of the term "extrusion temperature" by Dr. Phillips might cause some confusion. In the present paper extruded rod was used but it was cooled after extrusion and reheated for forging. It was the temperature of the latter heating that determined the condition of the alpha and the beta.

The hardness figures requested are:

ROCKWELL HARDNESS:  
B SCALE,  $\frac{1}{16}$ -IN. BALL, 100-KG. LOAD

	As Forged	After 1 Hr. Anneal at 450° C.
Transformed areas (all alpha).....	52 to 54	0 to 2
Untransformed areas (alpha and beta before annealing)...	57 to 60	19

The difference in hardness between forged and annealed samples has been attributed to the presence of submicroscopic particles of beta in the transformed alpha. This ignores the possibilities of work-hardening by the dies and hardening due to the internal stresses set up by rapid cooling. Kent<sup>4</sup> has shown that copper is work-hardened when forged from a temperature of 600° C. or below. These two possibilities will have to be considered before the hardening of the transformed alpha is attributed entirely to the presence of submicroscopic beta.

<sup>4</sup> W. L. Kent: Behavior of Metals and Alloys During Hot Forging. *Jnl. Inst. Met.* (1928) 39, 222.

## Variations in Microstructure Inherent in Processes of Manufacturing Extruded and Forged Brass\*

BY OGDEN B. MALIN,† STATE COLLEGE, PA.

(New York Meeting, February, 1932)

IN conducting the manufacture of extruded brass rods and brass forgings it has been noticed that there is considerable variation in the physical properties, particularly the machinability of different rods and forgings, even though the composition, working temperatures and method of manufacture remain the same. It is the purpose of this paper to attempt to establish the cause and extent of this variation, and also to determine whether variations in composition within certain defined limits influence hardness and machinability to any marked degree.

The writer believes that this variation probably is due to the variation in grain size of the metal, therefore the microstructures of several compositions under various conditions of working were examined in an effort to establish this as a fact.

### SURVEY OF PREVIOUS WORK IN STUDYING EXTRUSION DEFECTS

Very little has been published concerning defects in extruded and forged brass. In 1921, R. Genders<sup>1†</sup> delivered a paper before the British Institute of Metals, relative to a defect inherent in the extrusion process. This defect, commonly found in extruded brass rod, shows up in the form of a circle in a transverse section consisting of oxides and impurities, and is generally present in the last 25 to 30 per cent of the rod. Genders concluded that the defect is caused by the turning inward of the skin of the billet at the edge of the plunger because the inside of the billet is more plastic than the outside, which is in contact with the cooler container; the outside skin will lag behind to form the rear end of the rod. Genders suggested a movable die as a remedy, and while this met with fair success, it is not used in present practice.

About the same time as Genders' experiments, Tucker<sup>2</sup> and Rosenhain<sup>3</sup> conducted experiments using colored plasticene in the form of a billet, and found much the same defect as Genders. Dr. Rosenhain

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\* Part of a thesis by O. B. Malin on file in the library of the Pennsylvania State College.

† Assistant Professor of Metallurgical Engineering, The Pennsylvania State College.

‡ References are to bibliography at end of paper.

suggested the clamping of the rear end of the billet to the plunger to prevent movement of the outside surface in order to remedy the defect.

In 1930, R. L. Wilcox, under direction of the writer, conducted an investigation as to the cause of cold shuts forming in forged unions. In studying the macrostructure of several of these unions, he found that owing to the design of the die the metal folded back on itself, forming a cold shut at the corner. He also found, however, that the cold shuts

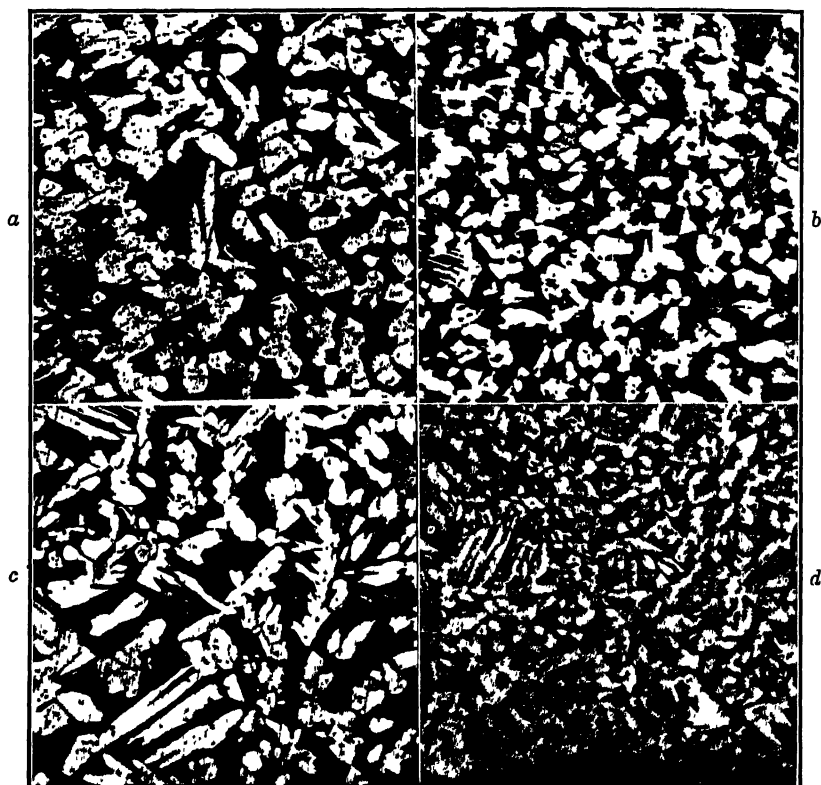


FIG. 1.—COMPOSITION A. Cu, 57.04 PER CENT; Pb, 1.99; Al, 0.16; Zn, REMAINDER.  
*a and b.*  $1\frac{5}{8}$ -in. rod; *a*, front end; *b*, rear end.  
*c and d.*  $3\frac{5}{16}$ -in. rod; *c*, front end; *d*, rear end.

formed in unions forged from metal with a fine grain while unions forged from coarse-grained metal did not exhibit this cold shut.

#### MATERIALS INVESTIGATED

In the work described in this paper billets of the compositions given in Table 1 were extruded to form rods  $1\frac{5}{8}$  and  $3\frac{5}{16}$  in. in diameter and were cut into slugs  $1\frac{1}{16}$  and  $1\frac{1}{16}$  in. long respectively. These were forged into

a valve stem and a union. All billets extruded and slugs forged were preheated to  $1450^{\circ}\text{F.} \pm 10^{\circ}$ .

Sections normal to the direction of extrusion were cut from slugs from the front end and also from the rear end of a rod of each of the compositions listed. Front and rear sections were cut from valve-stem forgings made from slugs cut from the front and rear of a  $1\frac{5}{8}$ -in. rod of each composition. Finally, front and rear sections were cut from union forgings made from the slugs cut from the front and rear of a  $3\frac{5}{16}$ -in. rod of each

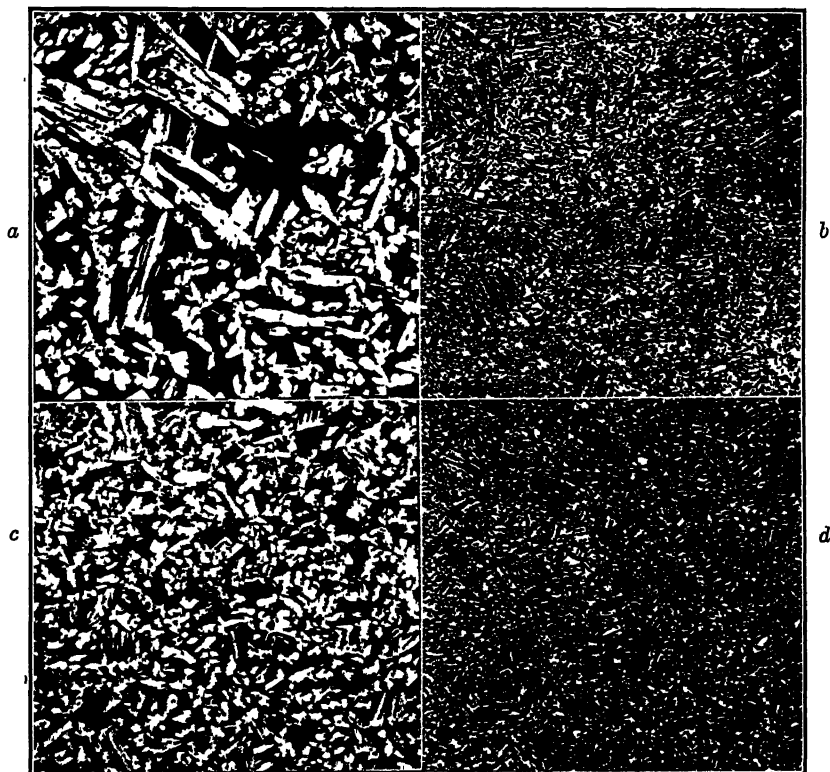


FIG. 2.—COMPOSITION A. Cu, 57.04 PER CENT; Pb, 1.99; Al, 0.16; Zn, REMAINDER.  
a and b. Stem made from front slug; a, front end; b, rear end.  
c and d. Stem made from rear slug; c, front end; d, rear end.

composition. This made 12 specimens for each composition. These were prepared for microexamination, using an ammonia-hydrogen peroxide etchant, and photomicrographs at 100 dia. were taken of each.

All compositions studied consist of a single solid solution, beta, at temperatures between  $650^{\circ}\text{C.}$  (plus or minus) to  $900^{\circ}\text{C.}$  Upon cooling below  $650^{\circ}\text{C.}$  a second solid solution, alpha, separates out in a beta matrix. The etchant shows the alpha as light crystals in a dark or black matrix of beta.



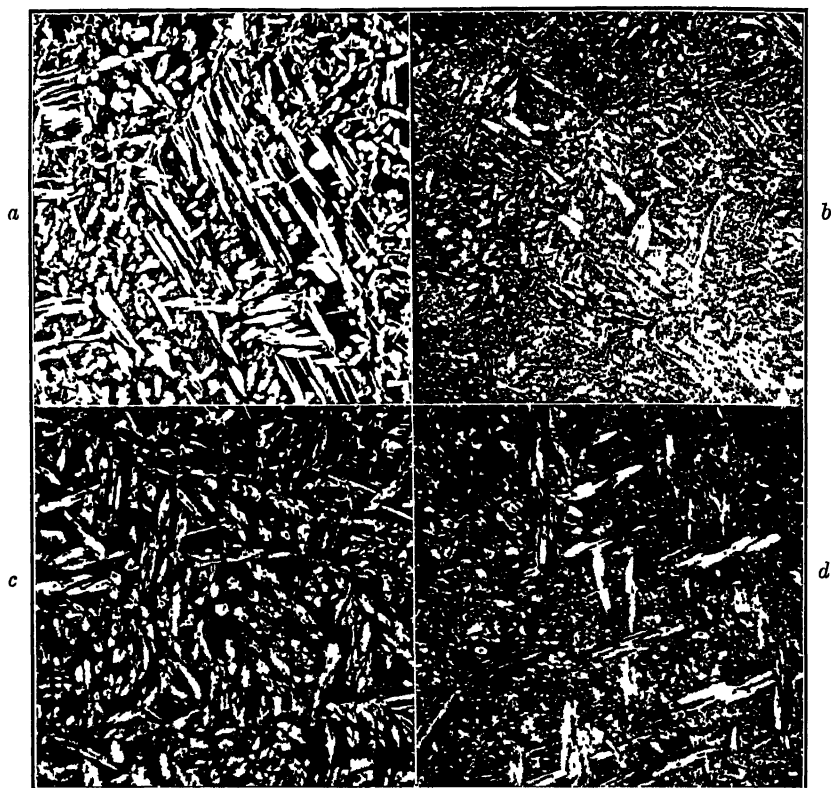


FIG. 3.—COMPOSITION A. Cu, 57.04 PER CENT; Pb, 1.99; Al, 0.16; Zn, REMAINDER.  
*a* and *b*. Union made from front slug; *a*, front end; *b*, rear end.  
*c* and *d*. Union made from rear slug; *c*, front end; *d*, rear end.

TABLE 1.—*Composition of Test Pieces*

Test Piece	Cu, Per Cent	Al, Per Cent	Pb, Per Cent	Zn
A	57.04	0.16	1.99	By difference
B	57.90	0.08	1.96	
C	58.30	0.08	2.17	
D	58.50	0.16	2.03	
E	58.76	0.16	1.96	
F	58.84	0.08	2.07	
G	58.90	0.16	2.17	
H	59.22	0.16	2.07	
I	60.30	0.16	2.29	

The photomicrographs (Figs. 1–6) deal with compositions A and I, although a similar set was made for each of the compositions, and without

exception showed the same variation in grain size. The other photomicrographs are embodied in the thesis mentioned at the beginning of the paper.

### DISCUSSION OF RESULTS

The structures of the slugs cut from the front end of the extruded rods are coarse grained while the structures of the rear slugs cut from the same

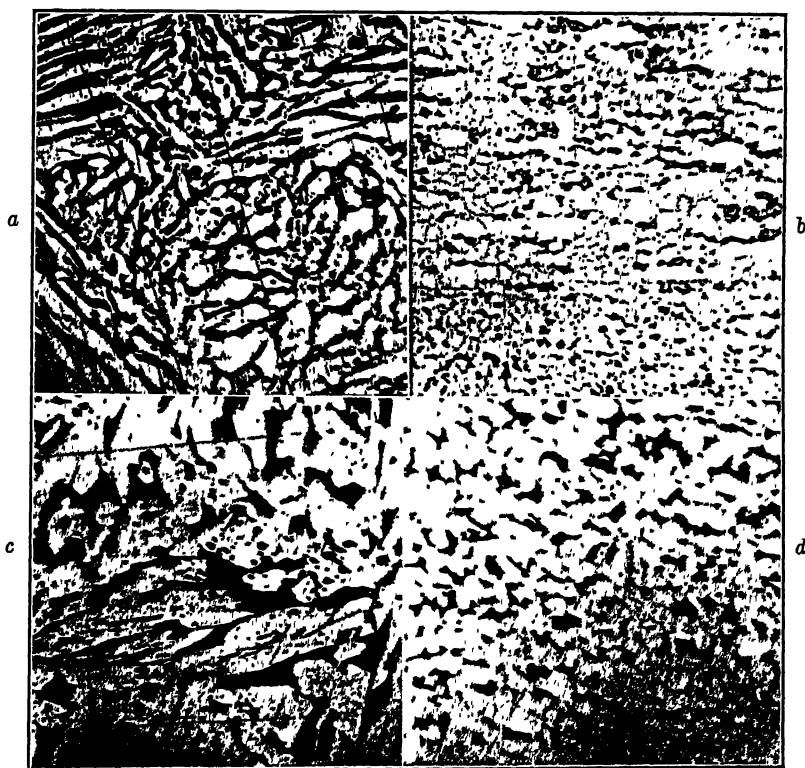


FIG. 4.—COMPOSITION I. Cu, 60.30 PER CENT; Pb, 2.29; Al, 0.16; Zn, REMAINDER.  
*a* and *b*. 1  $\frac{5}{8}$ -in. rod; *a*, front end; *b*, rear end.  
*c* and *d*. 3  $\frac{5}{16}$ -in. rod; *c*, front end; *d*, rear end.

rod are much finer. Undoubtedly this is due to the fact that the last part of the rod is extruded at a lower temperature than the first part, which causes the rear to receive a greater amount of mechanical work. According to Genders' theory, the last part of the rod is formed from the outside of the billet which has been cooled by contact with the chamber of the press, thus accounting for the lower temperature at which the rear end of the rods were extruded.

The photomicrographs of the valve stems show that while there is not such a marked difference in the structure of the stems forged from the front and rear slugs as there is in the slugs themselves, the stems made from the front slug have a slightly coarser structure than those made from the rear slugs. It is also evident from the photomicrographs that the front end of the stem has a slightly coarser structure than the rear

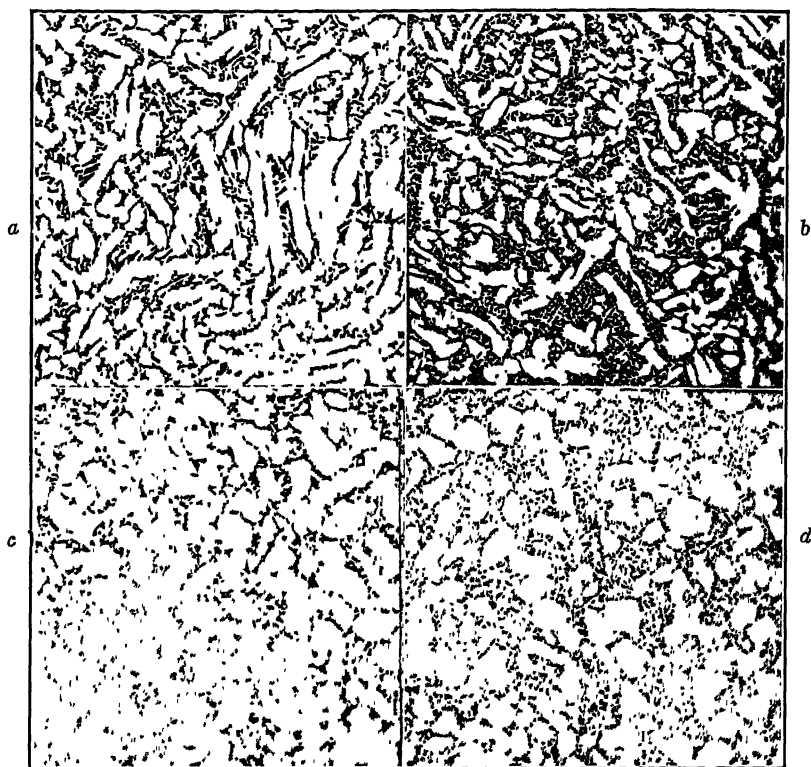


FIG. 5.—COMPOSITION I. Cu, 60.30 PER CENT; Pb, 2.29; Al, 0.16; Zn, REMAINDER  
*a* and *b*. Stem made from front slug; *a*, front end; *b*, rear end.  
*c* and *d*. Stem made from rear slug; *c*, front end; *d*, rear end.

of the same stem. The annealing of the slugs preparatory to forging should remove most of the difference existing in the structure of the slugs, but either the temperature has not been high enough or the time of annealing too short to remove all dissimilarity and produce an equilibrium structure.

The photomicrographs of the unions seem to show the same evidence as those of the stems, except that the differences in structure are less pronounced. As to the shapes of the respective forgings, the union being a shorter piece, there is less chance of pronounced difference

in working conditions of front and rear than would be the case with the stems.

The effect of the variation in chemical composition was not conspicuously marked in the microstructures. The photomicrographs of composition I (Figs. 4 to 6) show a different type of structure from those of composition A (Figs. 1 to 3). They show coarse alpha grains with

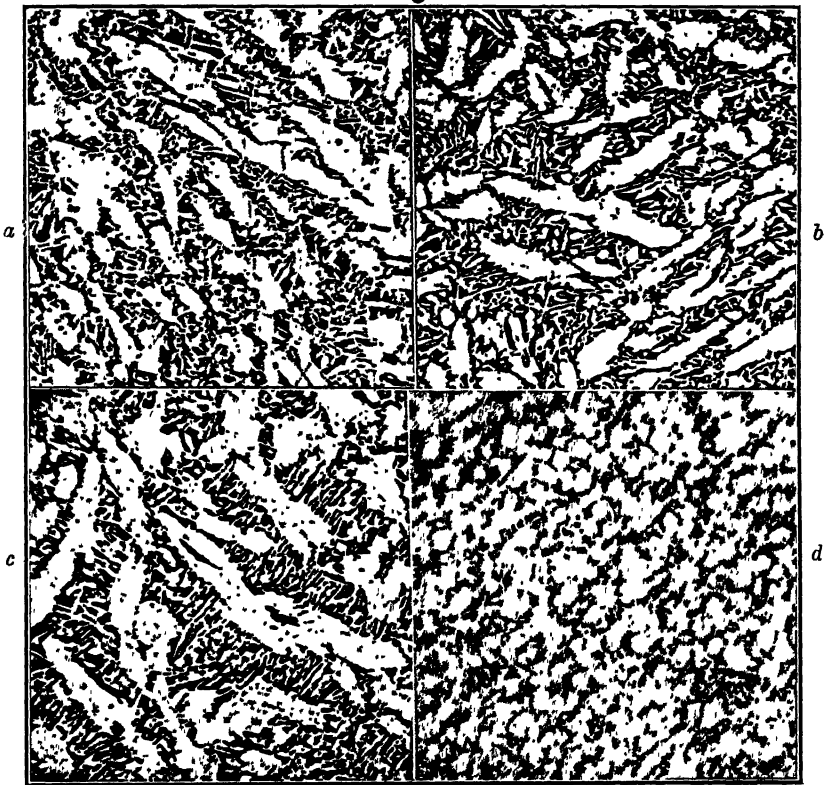


FIG. 6.—COMPOSITION I. Cu, 60.30 PER CENT; Pb, 2.29; Al, 0.16; Zn, REMAINDER.  
*a* and *b*. Union made from front slug; *a*, front end; *b*, rear end.  
*c* and *d*. Union made from rear slug; *c*, front end; *d*, rear end.

some broken-down alpha grains intermingled with fine beta. This apparently agrees with results in practice, for brass manufacturers have found that brasses of 60 per cent Cu or more are less easily forged than those from 57 to 60 per cent Cu, the higher alpha content making them less susceptible to hot work.

The variation in aluminum content being so slight, and the fact that it enters into solid solution, probably prevent it from having any effect upon microstructure.

## CONCLUSIONS

1. Slugs from the front ends of extruded brass rods of 57 to 60 per cent Cu content have a much coarser grain structure than those from the rear end of the same rods.

2. The front ends of elongated forgings of the same compositions have a coarser grain than the rear end of the same forgings.

3. The forgings made from the front slugs cut from an extruded rod have a coarser grain than the forgings made from slugs cut from the rear end of the same rod.

4. Variations in chemical compositions between 57 to 60 per cent Cu have little effect upon grain size of extruded rods or forgings made therefrom.

5. Small amounts of aluminum (0.08 to 0.16 per cent) added to brasses of 57 to 60 per cent Cu have no visible effect upon the microstructure. These additions have been found to cause the metal to fill out the die more fully.

6. Factory practice has shown that fine-grained structures are more difficultly machined than coarse-grained structures of the same chemical composition.

## FUTURE RESEARCH

Along the line of study just made, work could be done determining whether annealing would produce a uniform grain size in the product, and if so, the temperature and time of such anneal should be established. Investigation should also be made as to whether rear slugs would require a longer anneal than the front in order to produce uniformity.

## ACKNOWLEDGMENTS

The writer wishes to express his appreciation to the Titan Metal Manufacturing Co. of Bellefonte, Pa., whose whole-hearted cooperation made this work possible; to Messrs. Andrew V. Wetzel, Walter F. Nicoden and John W. Greagor for the preparation of some of the specimens and photomicrographs contained in this work; and to Dr. D. F. McFarland, of the Department of Metallurgy of the Pennsylvania State College, for his interest and helpful suggestions.

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## DISCUSSION

(John R. Freeman, Jr., presiding)

D. K. CRAMPTON, Waterbury, Conn.—Conclusion 4, that 57 to 60 per cent copper has little effect on the grain structure, does not seem to be in line with our experience. We find that it makes an appreciable difference. If the range were wider, say from about 56, the lower limit usually used, up to perhaps 64 per cent, a still greater difference due to copper content would be noted. In fact, if I interpret Professor Malin's pictures correctly, Figs. 1 and 4 bear out the contention just made, that there is an

appreciable difference in structure for rods of the same treatment due to differences in the copper content.

Conclusion 5 states that small amounts of aluminum added to these brasses have no visible effect upon the microstructures, but that they do tend to fill out the die more fully. Recently we have made a study of forging properties of various brasses, and among other things we find that for a given apparent copper content the best forging properties are obtained with straight copper-zinc alloys, not with additions of tin, aluminum or other elements that are sometimes used in such mixtures.

K. R. VAN HORN, Cleveland, Ohio.—The older theories of extrusion have been gradually revised to explain some of the more recent observations. Professor Malin referred to the studies of Rosenhain and Genders, who extruded colored plasticene clay billets. Later investigations, described in European periodicals, British Institute of Metals, etc., have shown that these original experiments were not entirely applicable to metals. Rosenhain's clay models showed that the entire core of the billet proceeded through the die and was then followed by the outside layers. Sections of the outside surface that had been oxidized might occasionally slip through the die, forming the observed oxide rings on extruded rod, but the majority of the original billet surface would be concentrated in the latter part of the rod. This metal would be cooled to a lower temperature, resulting in more cold work and consequent finer grain size.

According to some of the more recent contributions on the subject, this condition does not seem to exist. As the core proceeds through the die, metal is forced into the corners of the container adjacent to the die orifice. The core and then some of the outer layers pass through the die, with the accumulation of more metal at the front of the billet container surrounding the die. A shearing surface which serves as an excellent location for dross and inclusions to segregate is formed in order to permit the extrusion of the billet. Occasionally oxide particles are abraded from the accumulated metal by the flowing action and pass through the die, forming the observed external rings. Finally the metal and oxide concentrated adjacent to the die at the front of the container is forced through the opening. The majority of the oxide would then be located at the end of the extruded rod and the last metal would be more rapidly cooled by the container, causing more cold working at the end of the process. These theories easily explain Professor Malin's observations.

O. B. MALIN (written discussion).—Mr. Crampton's remarks concerning conclusion 4 refer to difference in grain structure whereas this conclusion in the paper speaks only of grain size. It is well known that brasses with more than 60 per cent Cu have a different structure than those below 60 per cent because of the increasing amounts of alpha and decrease of beta. This is shown by Figs. 1 and 4. However, variations in composition between 57 and 60 per cent Cu have little effect upon the size of grain when working conditions are the same. Photomicrographs substantiating this are embodied in the original thesis but do not appear in the paper on account of the cost of publication.

With reference to remarks on conclusion 5, it was found that in forging some complicated shapes from brasses without the addition of aluminum the metal failed to fill out corners in the die. When aluminum was added, the metal filled the die completely. This was then attributed solely to the aluminum, because composition and forging conditions were kept the same as far as was humanly possible.

The theory of the flow of metal during extrusion submitted by Dr. Van Horn varies little in substance and none at all in effect from that advanced by Rosenhain and Genders as quoted in the paper. These authors both state that the outside skin of the billet lags behind to form the rear end of the rod, but do not specifically state where the metal lags. Dr. Van Horn's statement may shed some light on the question as to where the metal stays while lagging.

# Relation of Crystal Orientation to Bending Qualities of a Rolled Zinc Alloy

BY GERALD EDMUNDS\* AND M. L. FULLER,† PALMERTON, PA.

(Boston Meeting, September, 1931)

THE development of "fiber" or preferred orientations, during the plastic deformation of metals, and the relation of such structures to the anisotropic characteristics of worked metals has become a subject of common knowledge among metallurgists. Very little has been published, however, relative to variations existent throughout the cross-sections of rolled strips,<sup>1</sup> and the influence that such variations may have. This paper presents such a study on a rolled zinc alloy.<sup>2</sup> The significance of small differences in surface structure is shown in relation to bending properties.

Experience with zinc and its alloys has shown that the outer radius of the bend, which is subject to tensile deformation, is the common region of failure. In considering relations of structural characteristics to bending properties it will suffice, therefore, to consider the ease and possible extent of tensile deformation resulting from various orientations. It is necessary in this connection to assume that on the average the individual crystals of a polycrystalline material act substantially as if their movements were unobstructed by the surrounding grains. This assumption is not strictly valid, but the error involved is unlikely to affect seriously the qualitative conclusions derived from its use.

The mechanism of the plastic deformation of zinc crystals has been described by Mark, Polanyi and Schmid<sup>3</sup> and by Mathewson and Phillips,<sup>4</sup> and is regarded as being accomplished by block movements or

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<sup>1</sup> Variations of structure throughout the cross-section of wire have been reported in the literature.

<sup>2</sup> This alloy contained, in addition to zinc, 1.0 per cent copper and 0.01 per cent magnesium. Its crystal form is hexagonal close packed, the same as that of pure zinc.

<sup>3</sup> H. Mark, M. Polanyi and E. Schmid: Vorgänge bei der Dehnung von Zinkkristallen. *Ztsch. f. Phys.* (1922) 12, 58.

<sup>4</sup> C. H. Mathewson and A. J. Phillips: Plastic Deformation of Coarse-grained Zinc. *Proc. Inst. Met. Div., A. I. M. E.* (1927) 143.

C. H. Mathewson: Twinning in Metals. *Proc. Inst. Met. Div., A. I. M. E.* (1928) 7.

The results of a further study of plastic deformation of zinc as related to twin-



slip along basal crystallographic planes, and, to a lesser extent, by twinning on pyramidal planes<sup>5</sup> of the form 10.2. Slip may occur in either sense along any one of three directions on the single set of basal planes and will account for enormous extensions of the crystal if favorably oriented. There are six sets of pyramidal planes on which twinning is possible, but this reorientation (by twinning) results from the action of stress in only one direction on each, and the maximum extension resulting from complete twinning is but 7.4 per cent. However, it is important to note that the reorientation of the lattice accompanying twinning may adjust a crystal to a position in which slip can occur, and in this indirect way permit a considerable extension. The application of these principles leads to a qualitative delineation of the orientations which will be unfavorable for the degree of extension required on the outer radius of a bend.

A crystal of which the hexagonal axis is coincident with the direction of extension has no stress component<sup>6</sup> tending to cause either basal slip or pyramidal twinning, and, as Mathewson and Phillips have stated, crystals in this orientation cleave along basal planes under small loads. No experimental tests have been made as yet on the alloy under consideration to determine at what angle from the direction of stress the hexagonal axis must lie in order that basal slip, rather than cleavage, will occur. Working with relatively pure zinc, Schmid<sup>7</sup> claims to have observed basal slip in a crystal of which the hexagonal axis lay at  $6^{\circ} 30'$  to the axis of tension. This value is doubtless below that for alloyed<sup>8</sup> and for polycrystalline<sup>9</sup> zinc.

Crystals of which the hexagonal axes are perpendicular to the direction of stress are almost ideally located for mechanical twinning on the pyramidal (10.2) planes, but this corresponds to but a slight elongation (less than 8 per cent) and reorients the crystals into positions in which these axes are inclined from  $4^{\circ}$  to  $30^{\circ}$  to the direction of stress, depending upon the angle between the latter and the normal to a first-order prismatic plane. As was explained in the preceding section, most of these orientations are more favorable for cleavage than for additional plastic deformation.

It can be shown that any crystal so oriented that its hexagonal axis is inclined at an angle other than approximately either  $0^{\circ}$  or  $90^{\circ}$  to the direction of tensile stress is in a position favorable for rather extensive

ning may be found in a more recent paper by E. Schmid and G. Wassermann: Über die mechanische Zwillingsbildung von Zinkkristallen. *Ztsch. f. Phys.* (1928) 48, 370.

<sup>5</sup> These planes lie at an angle of  $43^{\circ}$  to the hexagonal axis.

<sup>6</sup> The maximum shear stress in tension is at  $45^{\circ}$  to the direction of extension.

<sup>7</sup> E. Schmid: Discussion. *Proc. Inst. Met. Div., A. I. M. E.* (1927) 137.

<sup>8</sup> C. H. Mathewson: Discussion. *Proc. Inst. Met. Div., A. I. M. E.* (1927) 194.

<sup>9</sup> Z. Jeffries and R. S. Archer: *The Science of Metals*, 171. New York, 1924. McGraw-Hill Book Co.

elongation. The minimum deviation of the hexagonal axis from these positions that will permit sufficient deformation will be influenced by the purity and degree of strain of the metal, and the position of rotation of the crystal about the basal plane normal as an axis.

It is not intended to discuss here the effect on bending properties of such factors as microstructure, hardness, ductility and tensile properties. They have all been determined on many more specimens than are considered in this paper and *it has been found that good and poor bending metals frequently show no significant differences according to these tests, but when critically examined for preferred orientations invariably reveal dissimilarity.*

### TESTING OF BENDING QUALITY

As a means of determining bending quality, the dynamic cold-bend test has been used. The procedure<sup>10</sup> is simply that of hand-bending a specimen until its ends nearly meet and then completing the bend between the flat-faced adjustable plunger and flat bedplate of a bench press. Care is taken in the first operation to allow a sufficient radius to prevent localized straining. By setting the plunger of the press so that at the end of its stroke the distance between it and the bedplate is twice the thickness of the metal being tested, a flat bend is obtained, which is designated 2X. By increasing the plunger setting to three times the gage of the metal, a bend, designated 3X, with an inside diameter equal to the thickness of the metal is obtained, etc. The most severe bend at which no visible failure occurs determines the end point of the test. The determinations are usually made in two directions, *with* and *across grain*; that is, with the axes of the bends parallel and perpendicular, respectively, to the direction of rolling.

The bend-test values given in this paper are the averages of several determinations. The samples for orientation studies were selected from the centers of 6-in. squares. Eight bending tests were made on the surrounding material.

### X-RAY METHOD FOR DETERMINING CRYSTAL ORIENTATIONS

The monochromatic pinhole method was used in obtaining X-ray diffraction patterns. The X-ray apparatus was the multiple diffraction unit made by the General Electric Co., having a molybdenum target, Coolidge tube.

Two or three "reflection" and four "transmission"<sup>11</sup> patterns were required for a complete determination of the crystal orientations in any

<sup>10</sup> For a complete description of this test, the reader is referred to "Rolled Zinc," a Research Bulletin issued by The New Jersey Zinc Co. at its New York office.

<sup>11</sup> Two of the strips, for which complete orientation data are presented in this paper, were too coarse grained to give clear cut transmission patterns. A coarse-grained metal does not present a sufficiently large number of crystals properly oriented

one specimen. The several patterns were taken with the X-ray beam incident upon the specimen at definite, selected angles to the rolling plane and rolling direction of the strip.

In order to obtain thin sections, parallel to the rolling plane, for X-ray examination, the metal on both sides of the section desired was removed by etching. In carrying out the etching process, one surface was treated at a time, the other being protected from the action of the etching reagent with Picein wax, which could be applied at a temperature well below the recrystallization temperature of the alloy. The specimens were etched from the original (0.028 in.) gage down to a thickness of 0.008 in. with chilled nitric acid and the remainder of the way to 0.002 to 0.003 in. with a chromic acid-sodium sulfate metallographic etching solution. The latter reagent etches very slowly and evenly. When only 0.0005 in. was etched from the surface the chromic acid-sodium sulfate solution alone was used.

#### REPRESENTATION OF X-RAY RESULTS

For a satisfactory method of defining the systems of crystal orientations indicated by the X-ray diffraction patterns, the pole figure (*flächenpolfigur*) of Wever<sup>12</sup> was used. By this method a stereographic projection of the poles of a single atomic plane of the crystal lattice is made for all orientations found in the specimen. The figure including the projected points is the pole figure.

The basal plane (00.1), which is perpendicular to the principal axis of the zinc crystal, is the most convenient to project for a pole figure. The reasons for this are twofold: (1) The basal plane is unique in that there is only one set of planes of this form in each crystal. The translation of the X-ray diffraction data to the pole figure is thereby very much simplified; (2) basal plane slip plays an important part in the bending deformation, hence a pole figure of the basal plane orientations is the logical one for the problem at hand.

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in the path of a pinhole X-ray beam to give uniform diffraction arcs on the X-ray pattern. This difficulty was removed by using the technique of the "moving specimen holder." The device for continuously moving the specimen with respect to the X-ray beam was constructed in the instrument shop of the Research Division. Using this mechanism, a square area of the specimen  $\frac{3}{4}$  in. on a side traverses the X-ray beam, while the angular relationship between the X-ray beam and the rolling plane and rolling direction is preserved. The resultant pattern is similar to one from a stationary specimen of fine-grained metal and has the additional advantage that it is more representative of the entire specimen. In obtaining the reflection patterns a sufficiently large number of crystals contributed to render the usual technique for stationary specimens entirely satisfactory.

<sup>12</sup> F. Wever: *Ztsch. f. Phys.* (1924) 28, 69.

F. Wever: Texture of Metals After Cold Deformation. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 51.

The pole figures included in this paper have been drawn by projection upon the plane which includes the transverse or across rolling direction and the normal to the rolling plane. The rolling direction is normal to the plane of projection. A stereographic net,<sup>13</sup> having a radius of 2.5 in., has been found to be the most convenient device for making the projection. The plotted points indicated on the pole figures represent the limits of orientation ranges found on the X-ray patterns. The crosshatched areas include all projection points corresponding to crystal orientations present in the specimen. Where an area is doubly crosshatched, a region is indicated in which the crystal population is denser than in the singly crosshatched areas of that pole figure.

A basal plane pole figure does not define completely the orientations unless accompanied by the pole figure of some other plane. It so happened, however, that crystals were found in all possible positions of rotation about the basal plane normal as an axis. Hence, for the specimens treated in this paper, no pole figure other than that for the basal plane was required.

To one not familiar with the stereographic projection, the pole figures may not present a clear picture. The following, although not rigorously correct, may offer an understandable picture of the meaning of the pole figure and its derivation. Imagine a sphere, the center of which is a point in the metal strip whose orientation is being studied. Within this sphere, proceeding from the center and intersecting its surface, are normals to the basal planes representing all the orientations present in the strip. If the sphere is viewed along the rolling direction, the intersections of the basal plane normals with its surface will form a figure similar in shape and location to the stereographically projected pole figure.

It follows from the foregoing discussion that the distance of a point on the pole figure from the center of the figure is determined by the angle which the corresponding basal plane normal makes with the rolling direction. The position of this point with respect to the normal or transverse direction is an indication of the azimuthal position of the basal plane pole about the rolling direction as a pole.

#### X-RAY DATA REQUIRED FOR POLE FIGURES

A list of the X-ray patterns required to furnish orientation data for the pole figures presented in this paper is given in Table 1.

The reflection patterns furnish the data for those orientations in which the basal planes are approximately parallel to the rolling plane. The data for pole figure 1 are entirely from reflection patterns, as well as the corresponding areas on pole figures 2, 4 and 5.

These reflection patterns analyze the orientations to a depth not exceeding 0.0002 to 0.0003 in. below the surface of the specimen being

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<sup>13</sup> A. Hutchinson: *Mineralogical Magazine* (1908) 15, 93-112.

TABLE 1.—*X-ray Patterns Required for a Pole Figure*

Type of Pattern	Angles between Incident X-ray Beam and		
	Rolling Plane	Rolling Direction	Transverse Direction
Reflection. . . . .	8° <sup>a</sup>	90°	
Reflection.... ..	8°		90°
Reflection..... .	8°	40°	
Transmission. . . . .	90°		
Transmission. . . . .	50°	90°	
Transmission . . . . .	25°	90°	
Transmission. . . . .	25°		90°

<sup>a</sup> The grazing angle of incidence for basal plane diffraction is 8°.

examined.<sup>14</sup> The orientation data from reflection patterns, therefore, are representative of only a thin layer of the surface of the metal. This fact will be referred to more specifically in the discussion of the pole figures to be presented in the latter part of the paper.

Unlike the reflection patterns, the transmission patterns analyze the specimen throughout its entire thickness. They are required in order to furnish the data for the orientations in which the basal planes make large angles with the rolling plane. For such orientations the reflection patterns will not record basal plane reflections.

Some of the patterns designated in Table 1 furnish definite points for plotting on the pole figures while others merely serve to establish the absence of orientations in certain regions.

## RESULTS AND DISCUSSION

Preliminary orientation studies indicated that the crystal orientations found in the surface of a strip of this alloy largely determine the bending properties. When one considers that the maximum strain in bending occurs in the surfaces of the strip being bent, it is reasonable to expect this to be the case.

Examination of a large number of strips has shown that orientations may be present in the surface, down to a depth of 0.001 in. or less, which are unfavorable for bending deformation by basal plane slip. Experimentally it has been found that when this layer of unfavorably oriented crystals is as thick as 0.0005 in. or more, the specimen will have poor *with-grain* bending properties. The remainder of the specimen may have crystal orientations favorably located for both *with-grain* and *across-grain* bending deformation. The rolled alloy strips discussed in this paper show good *across-grain* bending properties. The across-grain bend tests

<sup>14</sup> This value was calculated from a consideration of the absorption of the X-rays in zinc and the angle of incidence of the X-ray beam.

are at the good bending limit of the test (2X) and hence the variation in across-grain bending could not be followed. The fact that the across-grain bends are never poorer than 2X, despite the presence of the unfavorable surface orientation, is probably due to the nature of the orientation directly below the surface layer. It will be shown later that the sub-surface orientations are more favorably situated for across-grain than for with-grain bending.

The surface orientation which was found to accompany poor bending properties is one in which the crystals are oriented with their basal planes approximately parallel to the rolling plane of the strip.<sup>15</sup> As has been stated in the introduction, this orientation is unfavorable for bending.

Fig. 1 is the pole figure for a typical case of this surface orientation. The shaded areas on this pole figure include all of the orientations present in such a typical surface layer. The loci of orientations in which the basal planes are in the position of maximum shear stress for across-grain and with-grain bends are shown on the figure.

The existence of this surface orientation was readily determined by means of reflection patterns. By etching away the surface of the specimen in small steps and by taking X-ray reflection patterns at each depth, the depth to which this orientation extends below the surface can be estimated.

In Table 2 the orientation data at the surface and 0.0005 in. below are given together with the with-grain<sup>16</sup> bending properties for 12 specimens of the rolled alloy. Three relative designations of the orientations found are used: (1) "strong," when apparently all of the crystals have their basal planes approximately parallel to the surface (Fig. 1); (2) "moderate," when some of the crystals have their basal planes approximately parallel to the surface, and about an equal number have their basal planes at 20° to 60° to the surface (Fig. 5); (3) "weak or absent," when no evidence is found of crystals having their basal planes approximately parallel to the surface (Fig. 3).

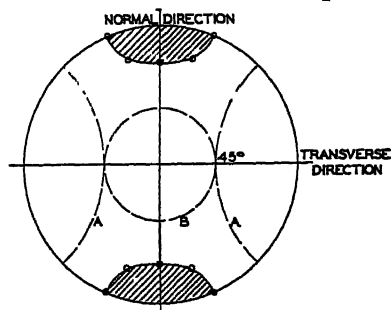


FIG. 1.—POLE FIGURE FOR TYPICAL SURFACE ORIENTATION.

A. Loci of orientations having maximum shear stress for basal slip during with-grain bending.

B. Locus of orientations having maximum shear stress for basal slip during across-grain bending.

<sup>15</sup> Independently Schmid and Wassermann [*Ztsch. f. Metallkunde* (1931) **23**, 87-90] have observed a somewhat similar surface orientation in rolled zinc. They appear to have made no attempt to correlate their orientation data with bending properties.

<sup>16</sup> The across-grain bends in all cases were 2X.

It is apparent from Table 2 that some of the unfavorable type of orientation was present to some extent at the surface of each specimen, but in the material with better bending properties little or none was observed at a depth of 0.0005 in., while in the poorer strips the unfavorable orientation was always found at that depth. From this it was reasoned that the thickness of this undesirable orientation has an important influence on the bending quality of the rolled alloy.

TABLE 2.—*Surface Orientation and With-grain Bending Properties*

Number of Specimen <sup>a</sup>	Concentration of Basal Planes Parallel to Rolling Surface		
	At Surface	0.0005 In. below Surface	Bend Tests
3155	Moderate	Weak or absent	2X
3158	Moderate	Weak or absent	2X
3281	Strong	Weak or absent	2X
3213	Strong	Weak or absent	2X
3142	Strong	Moderate	2X
3274	Strong	Moderate	2½X
3279	Strong	Moderate	2½X
3276	Strong	Moderate	3¼X
3265	Strong	Strong	3¼X
3280	Strong	Moderate	3¾X
3099	Strong	Strong	4X
3284	Strong	Moderate	4¾X

<sup>a</sup> All specimens listed are approximately 0.028 in. thick.

Having made this deduction it seemed advisable to obtain confirmation by determining the bending quality of metal from which the surface layer had been removed by etching. Conclusive proof of the detrimental effect of the surface orientation was obtained. A striking improvement<sup>17</sup> in bending quality was observed consistently, except, of course, those specimens originally at the good bending limit of the test. This is in complete agreement with the deduction from the orientation studies. Seventy other strips, chosen at random, for which orientation data are not available, were tested in the same way, yielding the results enumerated in Table 3.

The specimens on which orientation determinations were made, listed in Table 2, have undergone similar rolling procedures and have similar physical properties and grain size. Two of these specimens (3281 and 3284) were rolled according to the same nominal procedure and have

<sup>17</sup> It is recognized, of course, that bending properties improve with decreasing thickness but the effect is slight compared to the observed improvement noted after etching.

identical hardness, ductility and temper values,<sup>18</sup> but differ in surface orientation and in bending properties. They have been made the subject of a complete orientation study by the pole figure method.

TABLE 3.—*With-grain Bending Tests Before and After Removal of Approximately 0.001 In. from Each Surface*

Number of Specimens Tested <sup>a</sup>	Original Bending Test	Bending Test After Surface Removal
3	2X	2X
4	2 5X	2X
11	3X	2.1X
15	3 5X	2 6X
14	4X	2 6X
10	4.5X	3 5X
13	5X	4.2X

<sup>a</sup> All specimens are approximately 0.028-in. gage.

For this study two sections were prepared from each strip by etching as described earlier in the paper. The surface section extended to a depth of 0.002 to 0.003 in. The subsurface section extended from 0.0005 in. to 0.0025 to 0.0035 in. below the surface. The subsurface section is similar to the surface section except that it does not include the first 0.0005 in. of the surface layer, and that it extends to a greater depth.

An X-ray examination of these two sections gave the pole figures shown in Figs. 2 to 5. The reflection patterns were taken with the X-ray beam incident upon the surface side of the surface section and upon the side nearest the surface of the subsurface section. It is evident, therefore, that the portions of the diagrams in Figs. 2, 4 and 5, which correspond to those in Fig. 1, are representative of only a thin layer on the sides of the sections from which the reflection patterns were made.

With the exception of the orientation in which the basal planes are approximately parallel to the rolling plane, the pole figures indicate that the two specimens are very similar in crystal orientation. Consideration of Fig. 3, the subsurface section of No. 3281, shows that almost all the orientations represented are favorably situated for across-grain bends and many of them are favorably situated for with-grain bends. The unsuitability for bending of the surface orientations in both rolled strips is at once evident from the pole figures. No. 3284 has poorer bending qualities than No. 3281 because the unfavorable surface orientation is present to a greater depth.

It has been shown definitely that good bending quality is not found in this metal when a surface layer of crystals oriented with their basal planes

<sup>18</sup> For details of the test methods for hardness, ductility, and temper see reference of footnote 10.



approximately parallel to the surface extends to a certain depth. However, it is not to be inferred that a strip will have good bending properties merely because it does not possess this undesirable surface orientation. Using other rolling treatments, preferred orientations of other types are developed. Strips having dissimilar orientation characteristics and bending properties, unlike those upon which this paper was based, had different degrees of strain, so that the relation between orientation and bending properties is more obscure. Unfortunately, this later investigation has not progressed sufficiently to permit the formulation of conclusions as definite as those obtained in the studies just described.

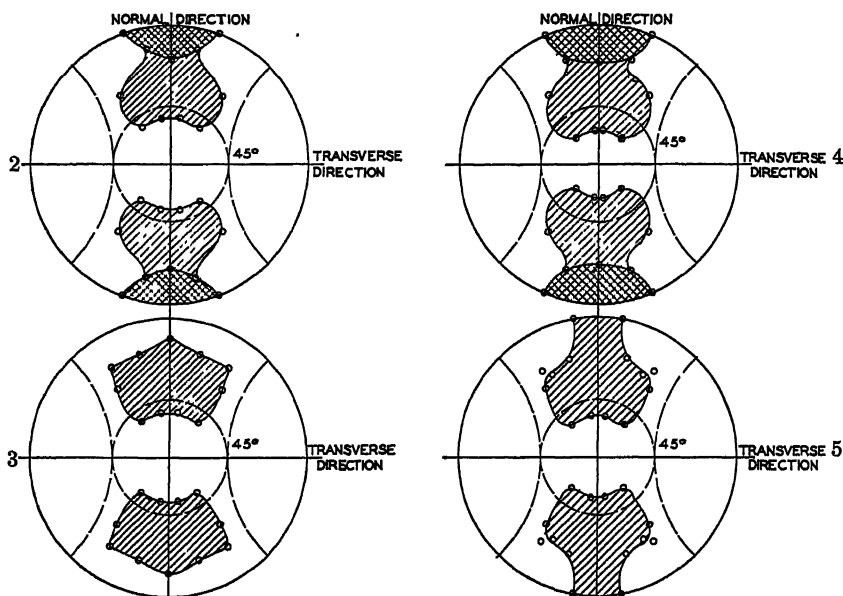


FIG. 2.—POLE FIGURE FROM SURFACE SECTION OF SAMPLE 3281.  
 FIG. 3.—POLE FIGURE FROM SUBSURFACE SECTION OF SAMPLE 3281.  
 FIG. 4.—POLE FIGURE FROM SURFACE SECTION OF SAMPLE 3284.  
 FIG. 5.—POLE FIGURE FROM SUBSURFACE SECTION OF SAMPLE 3284.

### SUMMARY

The relation of crystal orientation to the bending properties of zinc, both pure and alloyed, has been considered in the light of the explanation generally accepted for the mechanism of the plastic deformation of zinc. It has been deduced that two types of orientation are unfavorable for the bending deformations; namely, basal planes (1) parallel or (2) perpendicular to a line normal to the axis of the bend and lying in the surface of the strip.

Experimentally, the first type of unfavorable orientation has been observed as a thin layer at the surface of strips in a rolled zinc alloy.

Poor bending qualities were found whenever this orientation persisted to a depth of 0.0005 in. or more. Confirmation of this relationship has been obtained by determining the effect on bending properties of the removal by etching of the surface layer.

In addition, from a study of orientations beneath the surface, the cause of the better *across-grain* than *with-grain* bending properties has been determined.

#### ACKNOWLEDGMENT

The writers wish to express appreciation for assistance given by other members of the Research Division, New Jersey Zinc Co., during the course of the investigation and in the preparation of the manuscript.

#### DISCUSSION

(*E. M. Wise presiding*)

E. M. WISE, Bayonne, N. J.—Again it appears that etching is a good means for securing particularly good properties in metals. First, we found it offered a way to increase the fatigue limit of lead and now we find it is one way to make zinc that will withstand bending. Perhaps the authors might care to discuss the methods by which zinc possessing good bending properties may be made by rolling.

W. P. DAVEY, State College, Pa.—This paper is worthy of especial note because it is one of the few papers on X-ray metal research in which the interest lies in the end results rather than in the X-ray methods employed. It is a direct justification of X-ray research on metals, for it gives results which are immediately useful, so that the value of the X-ray work may be directly assayed.

It is evident from the results of this paper that a study of the relation of orientations and bending properties requires a study of orientations at *all levels* from the surface to the center of the specimen. In certain cases, the surface orientations become of enormous interest. It is not at all certain that this picture of the importance of surface orientation will apply rigorously to metals having more symmetrical structures than zinc, but in the absence of definite knowledge to the contrary we can hardly escape the temptation to generalize so as to try to magnify the importance of surface orientations in cubic metals.

The authors ought to be congratulated on having done an extremely important piece of fundamental work. We will hope that this will serve as a stimulus for further research and that it may be possible, either by the present authors or by others, to extend this type of work to the investigation at various levels from the surface to the middle of the specimen for other types of metals in addition to the work which has been done on zinc.

W. H. FINKELDEY, New York, N. Y.—The facts brought out by this interesting paper remind me of several instances of peculiar bending properties of rolled strip zinc. The peculiarity to which I refer was nearly always found in the heavier gages (0.040 to 0.060 in.) and consisted of a marked difference in the bending properties of the two sides of the strip. This difference could best be brought out by bending a number of samples cut from the strip a full 180° flat upon themselves, so that with alternate samples first one side of the strip and then the other was made the outside of the bend. The tests were made with and across the grain. The difference in the bending properties of the two sides of the strips was always more pronounced in the

specimens bent with the grain, and often it was possible to secure a satisfactory bend without cracking with one side of the strip, although the other side would show complete failure.

These bending properties apparently were dependent upon the character of the rolling treatment. Material exhibiting the two-sided effect was produced by breaking down the slab in the roughing mill to 0.056 in. and then completing the reduction to the desired gage (around 0.040 in.) in the finishing rolls. After considerable experimentation, it was found that the two-sided effect could be practically eliminated if the roughing operation were stopped at a thicker gage (about 0.075 in.) and the strip given more passes in the finishing rolls, using fairly moderate reductions.

In the light of the information given by the authors, a simple explanation for the peculiar bending properties which I have cited might be made on the basis that there is a surface layer of crystals favorably oriented to withstand bending stresses on one side of the strip, which is entirely absent or exists only imperfectly on the other side.

A. J. PHILLIPS, Maurer, N. J.—The authors might go one step further, and tell us how to prevent the phenomenon. In 1924 and 1925, when producing very large crystals of zinc by annealing close to the melting point, I found that the surface condition of a sample was always different from the interior condition; for example, large crystals, about 2 in. square by about  $\frac{1}{10}$  in. thick, were always found to be coated with a layer of small crystals on each surface. On one side the layer was thin, while on the other side it was often as much as 0.010 or 0.012 in. thick. Because of the association of the thick layer of fine crystals with the segregated lead in the zinc, we assumed without much justification that the fine crystals were due to the presence of lead interfering with the grain growth of the zinc. However, this was not borne out by the fact that the top surface of the sample, which was practically free from lead, also showed some fine crystals. I wonder whether this condition did not depend on the phenomenon described by the authors; that is, the original fine crystals along the surface of the sample were so oriented as to interfere unitedly with the growth of any invading crystal while the more randomly oriented crystals of the interior did not offer such resistance.

H. O'NEILL, Manchester, England.—The point which interested me most was the discovery that there is a difference in the preferred orientation of the metal as one proceeds from the surface towards the center of the rolled strip. It strikes me that for studies of this kind, recourse may be had not only to X-rays but also to the method of electron diffraction. In England<sup>19</sup> and America recently, the latter method has been brought into use. It has thus been possible to show that the polished surface of a metal appears to be more or less amorphous. From a carefully etched specimen, reflection of electrons gives diffraction rings which, when measured up, correspond to the space lattice of the metal. If, however, this surface is then carefully polished on a polishing pad, diffraction rings are not obtained but a diffuse radiation instead. This indicates that the crystalline structure of the surface metal has been destroyed.

The advantage of the electron method is that only a few tens of atomic layers are involved in the reflection process, whereas ordinary X-rays reflect from very many atomic planes below the original surface. Consequently, if anybody is interested in studying variations of preferred orientation from surface to center of a metal, electron diffraction may give some useful results.

W. P. DAVEY.—I have one more piece of information in connection with what Dr. O'Neill has said. At one time we tried, with X-rays of comparatively long wave

<sup>19</sup> G. P. Thomson: Analysis of Surface Layers by Electron Diffraction. *Proc. Roy. Soc.* (1930) **A128**, 649.

length, to investigate the orientation of a certain crystal of quartz. The crystal of quartz had been polished down in the customary way in order to make an optical surface, and it turned out to be no longer a single crystal but to be a poly-crystal, with a reasonably random orientation. After we had etched off the surface of the quartz with hydrofluoric acid, we found evidence of a single crystal and could get its orientation by X-ray methods. If polishing a rigid material like quartz can smear over the surface as much as that, it can be imagined what rolling will do to metals. I think it tends to illustrate the extreme importance of determining the orientation at the surface and at various layers below the surface.

E. M. WISE.—One thing I had in mind was the possibility of using extremely soft (long wave) radiation. Of course, it probably involves putting the plate in close proximity to or perhaps in the same chamber with the anticathode, but that is no serious matter.

This recalls some work that was done by Dr. Bozarth, in an investigation of the surface layers of oxidized steel (Bower-Bart finish). He was quite successful in determining the composition of extremely thin layers of compound formed on the surface of the metal by using the very soft X-rays.

One other thing came up in the course of the discussion which is very interesting; namely, the difference in the state of the two surfaces of the sheet. I happen to know of another situation of the same nature which perhaps is parallel. Material was being rolled; it came out with a very satisfactory surface on the top while the bottom surface invariably was checked. Evidently the checks developed in the rolling operation; certainly not in any previous heating operations. The answer to this thing was very simple—to alter the relative diameters of the top and bottom rolls. By making one roll smaller than the other, the difficulty was overcome.

G. EDMUNDS.—Mr. Finkeldey has brought out an interesting point which is rather common in metals; namely, a difference in the two surfaces of a piece of rolled metal. We have observed this in the past, and in some cases have made X-ray examinations and have found differences in the orientations. However, the work we have done along this line has been rather limited and we do not feel in a position to make an authoritative statement at this time. Another possibility we might suggest, however, is that the castings themselves may be responsible for that difference.

Mr. O'Neill has also brought up a point in regard to the electron diffraction studies. In the particular work that we have done it would hardly have been necessary to use electron diffraction methods in order to analyze a shallower layer of the metal, inasmuch as the X-ray merely analyzes a depth of about 0.0002 to 0.0003 in., and that is small in comparison to the 0.0005 in. which we have found to be the limit between good and poor bending material.

In some metals this might change and it might be desirable to apply electron diffraction methods which extend only to a few atom diameters in depth.

We would like to suggest that possibly some who are interested in other metals might make similar applications of these surface orientation studies which we believe are new.

F. WEVER, Düsseldorf, Germany (written discussion).—After Schmid and Wassermann found, some years ago, that the crystal orientation in a drawn wire shifts from the center to the outside, corresponding to macroscopic flow, it was expected that similar differences also must be present in rolled materials. Therefore it is gratifying to learn that Edmunds and Fuller have taken the trouble to make a thorough study of this displacement in the special case of hexagonal zinc. It is very interesting that their results again confirm the close relation, so frequently observed, between texture and mechanical action, and it appears advisable to point out that the study of metal

textures is important not only for the most prominent theoretical explanation of the mechanism of crystal deformation but also, because of the close relation between texture and flow of material during deformation and between flow of material and power consumed, it represents a valuable contribution to the technology of the deformation process.

E. SCHMID AND G. WASSERMANN, Berlin, Germany (written discussion\*).—The texture given for the middle layers of the sheet is excellent confirmation of what we have already found.<sup>20</sup> Fig. 6 shows the pole figure published by us in which the frequency of the position is indicated by the intensity of the shading. If Fig. 5 is shown

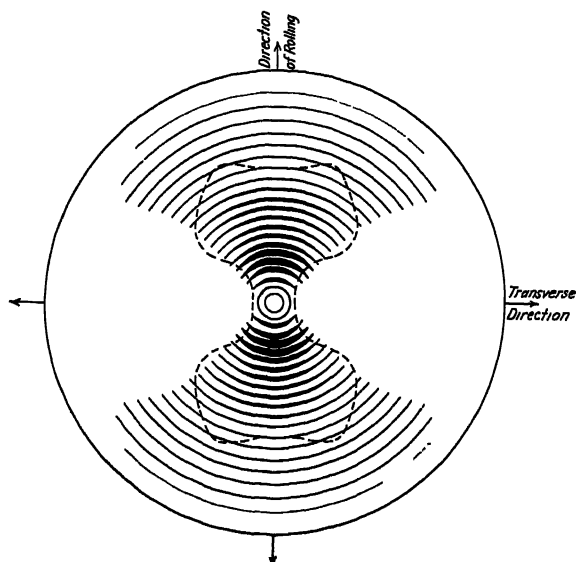


FIG. 6.—TEXTURE OF ROLLED ZINC, POLE FIGURE OF BASE.

in the usual manner (with the plane of the sheet as the plane of projection) we would obtain the region enclosed in the dotted line for the emerging points of the hexagonal axis. This agrees very well with our data. The differences in the region of lower frequency possibly depend on the type of working out the data (not taking into consideration small intensities) or differences in the preliminary treatment of the sheet.

Also, the nonhomogeneity of the texture in the different layers of the sheet which has been observed by us is confirmed by the investigation of Edmunds and Fuller. We found an even greater difference between the texture at the surface and inside.<sup>21</sup> Probably this depends on the weaker copper radiation used by us, with which the texture is shown in a thinner surface layer.

As the texture found at the surface of the sheet is present only in an extraordinarily thin layer, the crystal arrangement (Fig. 6) in the lower layers is essentially responsible for the properties of the sheet. Then, on the basis of the texture and the behavior of the single crystal we also could interpret a series of properties (elastic limit, tensile

\* Translated from the German.

<sup>20</sup> *Metallwirtsch.* (1930) 9, 698.

<sup>21</sup> *Ztsch. f. Metallkunde* (1931) 23, 87.

strength, elongation, modulus of elasticity, thermal expansion, electric resistance) in their dependence on the direction in the sheet. The very interesting determinations of Edmunds and Fuller on the bending properties of the sheet and their relation to the texture and single crystal behavior represent important progress in the understanding of the properties of polycrystalline technical metals. We wish only to point out that a basal position of  $45^\circ$  to the direction of elongation means a minimum of the plastic limit but not a maximum of the elongation, which should be essential in the bending tests that are described.

G. EDMUNDS AND M. L. FULLER (written discussion).—In reply to the discussion of Dr. Schmid and Dr. Wassermann, it may be stated definitely that the differences in orientations in the regions of lower frequencies as observed by them and by us are not due to any lack of consideration of the minor diffraction effects, but to differences in the composition or treatment of the materials. Our investigations, covering a wide range of treatments of rolled zinc and zinc alloys, have shown that the orientation characteristics of all layers of the strip are influenced radically by variations in rolling treatment. The texture shown by Fig. 6 has been observed in strip which we have examined. In consideration of the variety of textures developed in rolled zinc the agreement between the results of Schmid and Wassermann and ourselves is surprisingly close. In a very recent article Caglioti and Sachs<sup>22</sup> described a texture almost identical to the ones shown by our Figs. 4 and 5.

We are well aware that a basal position of  $45^\circ$  to the direction of elongation is not one resulting in maximum elongation, but, as stated in the paper, is the position of maximum shear stress along the basal planes. Obviously, for any one crystal the position favoring maximum elongation is that in which the inclination of the basal plane to the direction of strain is the greatest at which cleavage does not occur. In the light of available data it would, of course, be impossible to define the mean orientation most favorable to good bending of a rolled strip where the individual crystals of the rolled strip differ considerably in orientation. Even if the individual crystals were assumed to act as if uninfluenced by boundaries or neighboring crystals, it would still be necessary to know the volume distribution of the various orientations and the range of angles to the direction of stress at which slip occurs in preference to cleavage or twinning in zinc of the particular composition under consideration. Calculations of the capacity of a crystal for extension by basal slip alone, however, indicate that the range of mean orientations suitable for good bending is wide, and that it is only necessary that not too many crystals lie in the unfavorable positions already discussed.

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<sup>22</sup> v. Caglioti and G. Sachs: Die Walztextur von Zink und Magnesium. *Metall-wirtsch.* (1932) 11, 1-4.

## Structure of Cold-drawn Tubing

BY JOHN T. NORTON\* AND R. E. HILLER,† CAMBRIDGE, MASS.

(New York Meeting, February, 1932)

THE tremendous increase in the use of metals that have been prepared by the various cold-working processes during recent years has greatly stimulated the investigation of problems concerned with the fundamental nature of these processes. It has been observed in practice that different methods of bringing about the same dimension changes in a sample result in a rather wide range of properties. Cold working reduces the ductility of a metal, or what is perhaps more nearly correct, its "working capacity," and naturally the manufacturer wishes to produce an article that has as large a working capacity as possible, and to produce it with the smallest number of operations. It has also been known for some time that cold deformation produces a parallel alignment of the crystal grains of a metal, and that the type of this preferred orientation depends to some extent at least upon particular processes employed in the deformation. The present investigation has for its purpose the study of the relations between the various factors of a cold-working process and the preferred orientation of the metal crystals resulting from this deformation. The work is chiefly confined to a study of cold-drawn seamless tubing.

### PREPARATION OF SAMPLES

The tubing samples used in this investigation were made of steel having a carbon content of 0.10 to 0.20 per cent, and were drawn on a standard type of draw bench. In order to obtain the large reductions, the annealed stock was coated with lead, for purposes of lubrication. The reductions of area stated refer to reduction from the annealed condition without intermediate heat treatment. The cold work was done as nearly as possible at room temperature. The samples of wire and strip used for purposes of comparison were of steel of approximately the same carbon content and were prepared in the manner indicated.

### X-RAY METHOD OF INVESTIGATION

The condition of preferred orientation in cold-worked samples is best investigated by the X-ray method that employs a small circular beam of

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rays which pass through the sample and fall upon a flat plate. It is usually known as the "pin-hole" method. It is shown schematically in Fig. 1, and the actual apparatus, which is of conventional type, is shown in Fig. 2. In the present work, an X-ray tube with a target of molybdenum has been used and the beam rendered monochromatic by means of a  $ZrO_2$  filter. The sample thickness in the case of iron was 0.003 in. and the sample to film distance was 4 cm. Under these conditions, an exposure of between 30 and 40 hr. is necessary. In order to obtain a picture of a particular section, the sample is cut in the plane of that section, and the X-ray beam is perpendicular to it. Thus the picture of a transverse section means that the X-ray beam is parallel to the tube axis. The pictures are mounted so that the direction of drawing or rolling is horizontal.

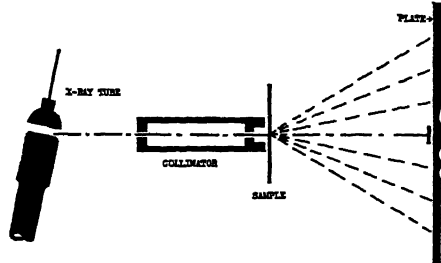


FIG. 1.—DIAGRAM OF APPARATUS.

When a sample has completely random orientation and rather coarse grain, such as are found in annealed material, the pattern consists of many small spots arranged more or less in rings. Fig. 3 is a pattern of this type which represents the annealed stock from which the tubing was

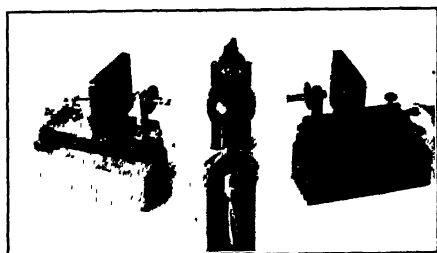


FIG. 2.—APPARATUS IN POSITION, SHOWING THE TWO CAMERAS.

drawn. As a rule, in cold-worked samples the grain is very fine, and here the pattern consists of smooth concentric rings. If the arrangement of grains is random these circles are of uniform intensity around the circumference, but if there is a parallel alignment, the blackening of the circles is concentrated in definite areas, and the more exact the alignment,

the narrower and more sharply defined are these areas. Fig. 5 shows pictures of fine-grained samples with random and with parallel orientation. The central white spot is the shadow of a lead disk set in the center of the film to intercept the direct beam and prevent general fogging of the film. The diffuse ring near the center is the reflection of the general radiation which has not been removed by the filter. The three sharp rings are the important portion of the pattern. The inner dark one is the reflection of the main beam from the 110 planes, which are the ones having the largest spacing and the densest atomic population. For this reason they give a very strong reflection at this small angle. The next outer ring is the 200 reflection, which is fainter, and the third ring is that due to the 211 planes.



A consideration of these three is sufficient for an analysis of the type of preferred orientation.

### PLASTIC DEFORMATION OF METALS

Extensive researches on cold-worked substances have established the fact that metals deform by a process of slip along planes of atoms in the crystal grains. Metals are crystalline and have their atoms arranged in a regular fashion, so that one may consider that all of the atoms of a particular grain lie upon a family of planes equally spaced and parallel. There are many such families, but it has been shown that those of easiest slip are the families with the largest separation, and the densest atomic population in the planes themselves. In body-centered cubic metals, such as iron, the planes of largest spacing are the 110 or dodecahedral

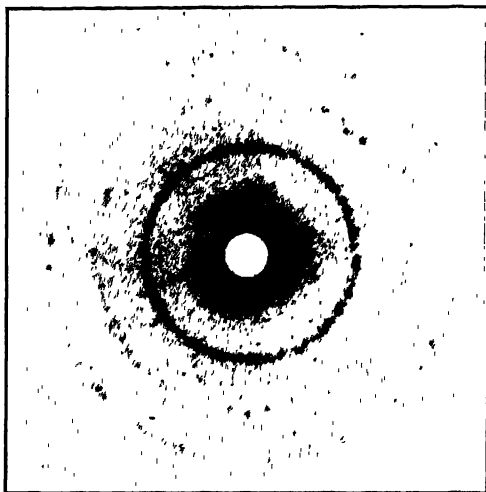


FIG. 3.—PATTERN OF ANNEALED METAL.

planes, and it is these that are principally involved in the deformation process. The progress of slip is always accompanied by a change in orientation<sup>1</sup> of the slip planes, and they are rotated toward the direction of extension. There are, however, six families of 110 planes making definite angles with one another upon which slip is possible, and slip will start on the set which is in the most favorable position with respect to the direction of tension. It can be shown that this position is approximately at 45° to the tension axis. As a result of the gliding, this set rotates toward the axis and another comes into the favorable position, so that the slip is transferred to it. After considerable cold reduction, the final orientation is one in which the 110 planes are arranged symmetrically

<sup>1</sup> J. T. Norton and B. E. Warren: Plastic Deformation of Metals. *Proc. Inst. Met. Div., A. I. M. E.* (1927) 350.

with respect to the direction of tension or elongation. This position is one of equilibrium, because if slipping causes a deviation from it the slip is transferred to another set of planes in such a way as to bring it back again.

If the deformation process is of such a nature that the sample is elongated principally in one direction, the crystal grains will have symmetrical positions with regard to this direction, but in a plane normal to this direction the alignment is not determined, and may be completely random. On the other hand, if the elongation has taken place simultaneously in two directions, so that the tension axis has two components, the orientation is limited with respect to both of these directions, hence is definitely fixed.

Since it is not the tension in the sample but the actual flow of metal that is the aligning force in cold-worked samples, the factors that govern the flow have interest. The relation between the direction of flow and the

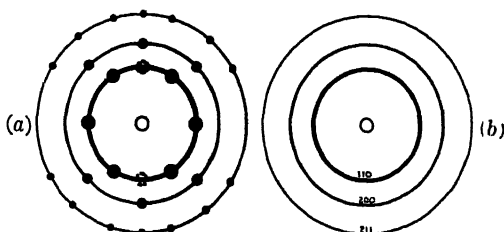


FIG. 4.—IDEAL PATTERN OF COLD-DRAWN WIRE. *a.* LONGITUDINAL. *b.* TRANSVERSE.

directions of elongation and tension in the sample is not at all clear at first sight. In tubing, the process is one of elongation in length and reduction in cross-section, so that a consideration of the somewhat simpler situation in wire and sheet which are reduced in a similar manner will be of considerable assistance.

### STRUCTURE IN COLD-DRAWN WIRE

The "fiber" structure or preferred orientation in iron wire has been studied by many investigators, and it has been definitely shown that the crystallites are so arranged that they each have a 110 axis, which is normal to a 110 plane, parallel to the axis of the wire, but that the orientation about this axis is a perfectly random one. Fig. 4 shows the ideal X-ray pattern to be expected from such an arrangement, and Fig. 5 is the pattern actually obtained.

During the drawing of wire, the elongation and tension are in the direction of the wire axis while the cross-section is reduced uniformly in all directions. Thus the direction of flow of metals seems to be along the wire axis. Wever<sup>2</sup> has pointed out that in the case of cubic metals

<sup>2</sup> F. Wever: Texture of Metals after Cold Deformation. *Trans. A. I. M. E., Inst. Met. Div.* (1931) 51.

which are cold deformed, the planes of largest spacing tend to set themselves at right angles to the direction of flow. Since in the wire the 110 planes are at right angles to the axis, it is clear that this axis is also the direction of flow, hence there is no other aligning tendency. Thus the wire should show, as it does, the random orientation about the axis.

#### STRUCTURE IN SHEET

The arrangement of the crystallites in cold-rolled sheet is such that one set of 110 planes is parallel to the direction of rolling and at right angles to the plane of the sheet, while a second set is at right angles to both the direction of rolling and the plane of the sheet. Fig. 6 is the X-ray pattern calculated from this structure, while Fig. 7 is the actual pattern obtained. They are in reasonable agreement. The sheet

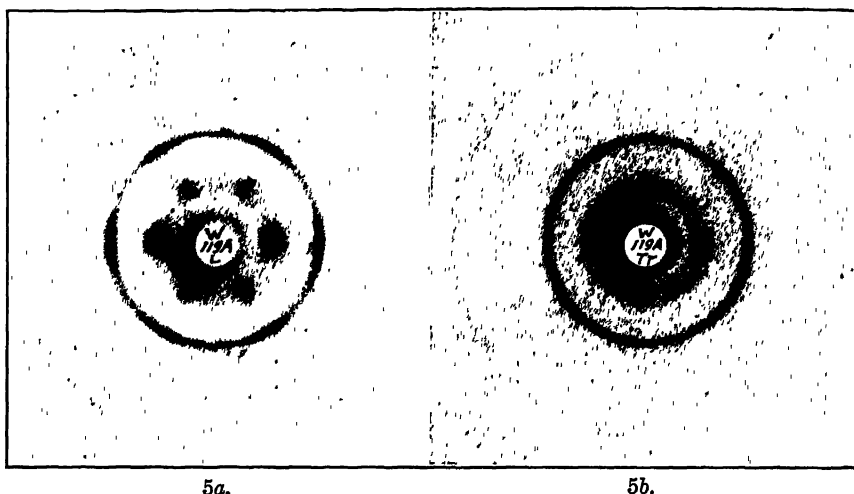


FIG. 5.—ACTUAL PATTERN OF COLD-DRAWN WIRE. *a.* LONGITUDINAL *b.* TRANSVERSE.

during rolling is elongated and its thickness is reduced, but the width remains practically unchanged. To account for this structure there must be an alignment parallel to the elongation, and in addition an aligning tendency, hence a flow of metal sideways in the sheet as well as lengthwise. It is difficult at first to see why this should be because there is no sideways elongation. Assuming that the strip was given the same reduction in area by plain tension, it is clear that the width and thickness would both have been reduced, but actually the width was kept constant by the friction of the roll surfaces, and this must have produced what is, in effect, a tension sideways in the sheet which overcame the forces tending to reduce the width. Thus, speaking relatively, there was a sideways flow in the sheet and the alignment in this direction is the result. In a sheet the crystallites have a definite orientation which they

all approach with increasing amounts of cold work, while in the wire they tend to be parallel to one direction only.

Theoretically, the X-ray pattern of a longitudinal and a transverse section should be the same. Actually they are not as Fig. 7 shows, but the difference is one of degree, and is due to the different magnitude of the aligning tendency in two directions. It has been assumed that slip takes place only on the 110 planes, but actually the 200 planes also take part to a limited extent, which causes a slight modification of the pattern. However, the X-ray patterns obtained confirm the essential features of the assumed structures.

### STRUCTURE IN TUBING

In the discussion given above, the production of preferred orientation during the process of deformation has been based upon the idea of flow of metal due to dimensional changes in the sample, and the aligning tendencies of this flow. From a dimensional point of view, tubing may be considered as sheet without edges. The circumference of the tube

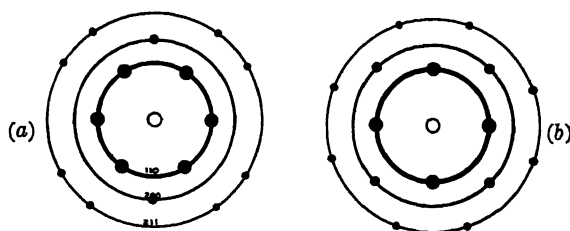


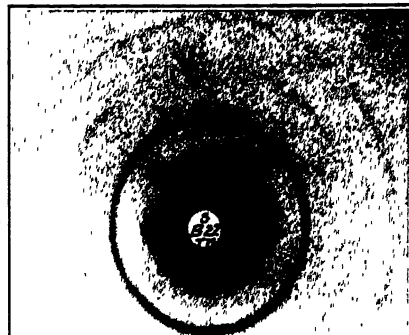
FIG. 6.—IDEAL PATTERN OF COLD-ROLLED SHEET.

- a. Longitudinal and transverse.
- b. Parallel to plane of sheet.

corresponds to the width of the sheet, and the wall thickness to the thickness of the sheet. If this idea is correct, a sample of tubing that has been reduced from the annealed condition in wall thickness only should show the same type of structure as sheet. The length has been increased, the thickness decreased, and the width remains unchanged, and these are exactly the conditions in reducing sheet. The photographs in Fig. 8, of the three sections of a tube reduced principally in wall thickness, show that the sheet type of structure exists when compared with the pictures of an actual sheet such as are shown in Fig. 7. It is rather difficult in drawing tubing to get a large wall reduction without reducing the circumference somewhat, so that the reduction ratio is not quite as great as in the sheet, but the equivalence of the two patterns is immediately evident.

Ordinary tube-drawing practice involves a reduction in both wall thickness and circumference, and it is of interest to investigate this more general condition. The most obvious case is that in which there has

7a.



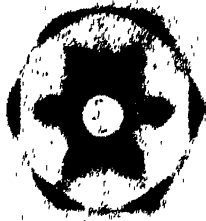
8a.



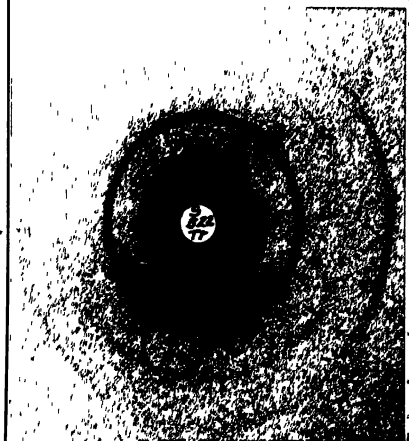
7b.



8b.



7c.



8c.



FIG. 7.—ACTUAL PATTERNS OF COLD-ROLLED SHEET.

FIG. 8.—PATTERNS OF TUBING WITH PRINCIPAL REDUCTION IN WALL THICKNESS.

a. Tangential. b. Longitudinal. c. Transverse

been an equal percentage reduction in circumference and in wall thickness. The situation here is practically identical with that of the wire. A small element parallel to the tube axis has been elongated, and its cross-section reduced equally in two right-angular directions. In a wire, a small element in the center is elongated, and the cross-section is also reduced equally in two right-angular directions. The dimensional changes are of the same relative magnitude, and the structures should be the same. Fig. 9, views of a tube with equal reductions in wall thickness and circumference, indicates by comparison with Fig. 5 that the structures are the same. In drawing wire, the conditions of deformation are symmetrical with respect to the wire axis, but in tubing with a die outside and mandrel inside the conditions are not exactly symmetrical as far as a line parallel to the tube axis and lying in the wall of the tube is concerned. For this reason the alignment of the crystals is not exactly parallel to the tube axis, so that the transverse section of the tube does not show a completely random orientation, as does the center of the wire. This difference, however, is of a minor nature, and does not affect the validity of the conclusions.

The influence of the amount of cold reduction upon the degree or exactness of preferred orientation is important, and has been studied by the examination of

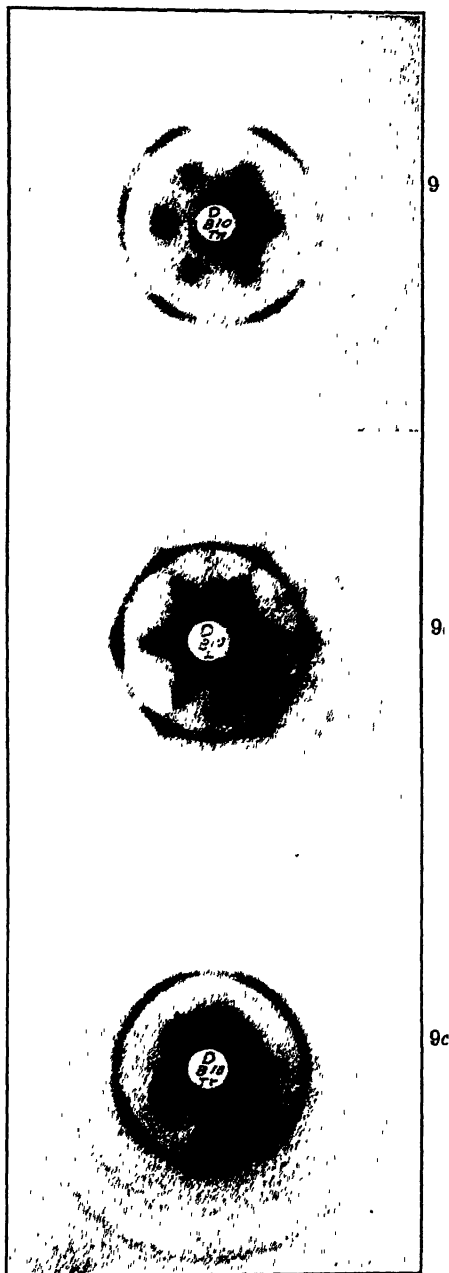


FIG. 9.—PATTERNS OF TUBING WITH EQUAL REDUCTION IN WALL AND CIRCUMFERENCE.

a. Tangential. b. Longitudinal. c. Transverse.

samples taken during the various stages of the drawing process. The results of this work show that the alignment parallel to the direction of extension—in this case the tube axis—increases in exactness with the increase in length or with the reduction in area of cross-section, which is, of course, proportional to it. The exactness of alignment at right angles to the tube axis is found to depend upon the relative changes in the wall thickness and circumference of the tube. A more general statement is that the degree of preferred orientation shown by a certain section of a cold-worked sample is a function of the ratio of the dimension changes of that section. If the two dimensions changed equally, no preferred orientation would be found, but if the change in one far exceeds the other, as, for instance, when one increases and the other decreases by a substantial amount, the preferred orientation will be nearly exact. This

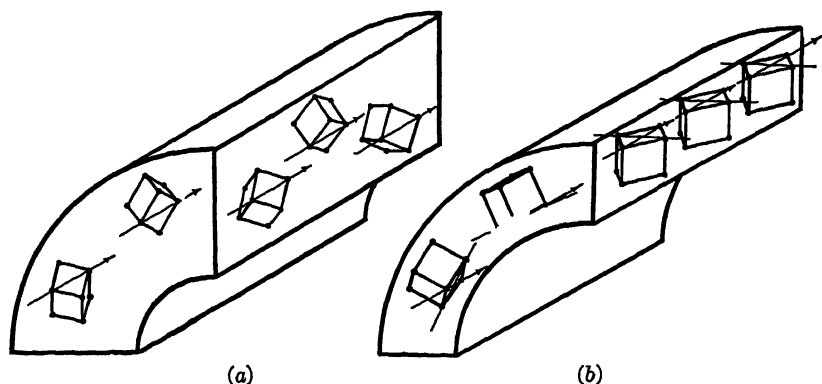


FIG. 10.—ORIENTATION OF CUBIC CRYSTALLITES IN TUBING.  
a. Equal reduction in wall and circumference.  
b. Reduction principally in wall thickness.

general statement applies not only to tubing but to other cold-worked shapes.

The results of this investigation present the following picture of the situation in cold-drawn tubing. As the length is increased, the crystal grains are broken up and aligned so that a 110 axis of each crystal is in the general direction of the tube axis. At the same time, if the wall thickness is being reduced more rapidly than the circumference, the crystals are also aligned so that another 110 axis in each crystal, at right angles to the first, becomes parallel to a tangent to the tube wall. Fig. 10 shows the orientation of cubic crystallites in these two kinds of reduction. Tubing reduced so that the dimensional changes are between these shows an intermediate structure. As long as the ratio of reduction in wall thickness to reduction in circumference is less than about 2, the wire structure is found. The sheet structure is definite when the ratio exceeds 2.5. Preferred orientation becomes evident at about 20 per cent total reduction of area and increases with further reduction.

## DEPENDENCE OF STRUCTURE ON METHOD OF REDUCTION

The reasoning employed above has not taken into account the dependence of the structure upon the particular method employed in reducing the samples. Results from rolled sheet and drawn wire have been directly compared with the tubing, and the question arises as to the equivalence of the results of these different processes. In order to

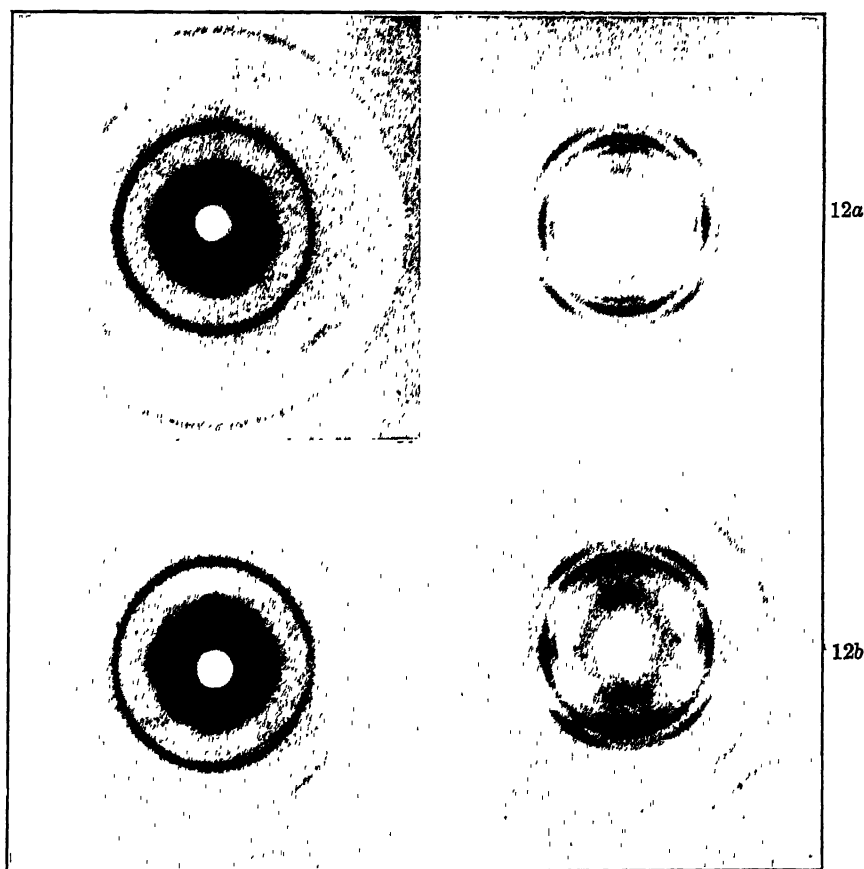


FIG. 11.—COMPARISON OF (a) ROLLED AND (b) DRAWN STRIP OF IRON.

FIG. 12.—COMPARISON OF (a) ROLLED AND (b) DRAWN STRIP OF ALUMINUM.

settle this question, samples of two other processes of tube reducing were compared with cold-drawn samples of the same degree of reduction. These samples were prepared by two processes, one of which was essentially a swaging and the other a rolling process.

The agreement is practically complete both as to type and degree of preferred orientation. As a further confirmation, samples of strip with a high degree of reduction were prepared by rolling in the ordinary way and



by drawing through a flat die. Both iron and aluminum were used. The results shown in Figs. 11 and 12 show the exact equivalence of these two modes of deformation, which produce the same dimensional changes. It has been known for some time that drawn wire and wire reduced by plain extension show the same structure. Hence it may be concluded that the type of preferred orientation in a cold-worked material depends only upon the dimensional changes which have taken place and not at all upon the particular process employed. It must be pointed out that at present experimental verification is available only in the case of simultaneous change in dimensions. There is no evidence to show that if the deformation takes place in different directions separately, the result is equivalent.

It is well known, of course, that different commercial cold-working processes involving the same dimensional change give very different results. In the light of the present work it seems as though the difference must be due to surface conditions and that these depend upon friction between the metal and die or roll. The pressure requires the interior of the metal to flow, but restrains the surface, and differential stresses may reach the point, in the region just below the surface, where failure of the metal results. Once the failure starts, further reduction is impossible. Or it may be that the metal has received such a severe deformation in this region that the additional deformation of bending or forming in service will cause failure.

All of the commercial processes which have been successful in obtaining high reductions without annealing, or ductile products after high reduction, have lessened this surface friction either by decrease of bearing area, lubrication, or diminution of bearing pressure. The metal-coating processes are examples of the first; the strip mills with small, backed up working rolls are examples of the second. The use of tension such as is employed in the Steckel mill has the effect of reducing the roll pressure, and hence the roll friction, because it introduces stresses in the body of the metal which act in the same direction as the roll pressure. If these stresses are nearly large enough to cause deformation only a slight additional roll pressure is needed for the rolling operation. With small-roll strip mills using tension on the strip, reductions are possible which are far outside the range of the older type of large-roll mills, yet the structure for equal reductions as shown by the X-ray methods is exactly the same. We are forced to look elsewhere for the difference and the surface seems the best place to look. Unfortunately, no evidence is yet available.

#### SUMMARY

The results of this investigation indicate that in cold-drawn low-carbon steel tubing the structure is intermediate between that of a wire

and a sheet. If the reduction in wall thickness and circumference are essentially of the same magnitude, the crystals are aligned so that each has a 110 axis parallel to the axis of the tube, but the arrangement is random about this axis. This is equivalent to the structure in wire. In case the tube has been reduced largely in wall thickness, the structure is similar to that found in sheet, and the crystallites are arranged so that a cube face is parallel to a plane tangent to the tube wall, and a 110 axis is parallel to the tube axis. The results have indicated also that the structure is independent of the method of reduction, and depends only upon the dimensional changes which have taken place during the reducing process. The differences in the products of various reduction methods are ascribed to surface conditions rather than to interior structure.

#### ACKNOWLEDGMENT

The authors wish to express their indebtedness to the Babcock & Wilcox Tube Co., which sponsored this research.

#### DISCUSSION

*(Arthur Phillips presiding)*

J. T. NORTON.—I am aware that the structure which I have presented as deduced from the X-ray photographs is too simple to represent the true state of affairs. There are factors in this extremely complicated problem of plastic deformation which have not been taken into account. I have considered only the structure which is a first approximation of the real one, in order that we may have a simple, practical working picture to deal with. In view of that I might add, however, that the two important conclusions to be drawn from this paper—namely, that the structures produced are independent of the means used in producing the reduction and that the structure produced is dependent only upon dimensional changes—are quite independent of whatever deductions we may make from the diffraction patterns themselves. We need only to make the assumption that like structures are to be deduced from like diffraction patterns.

I have made the observation that in connection with this work the vast differences found in the products of different reduction methods may be ascribed to conditions on the immediate surface of the sample. The work, I think, shows that the interior structure is the same regardless of the method. During my absence Mr. Hiller, the coauthor of this paper, made some observations from sections of thick wall tubing extending from the center of the tubing right to the surface. These sections are some  $\frac{3}{1000}$  in. thick, the outside section representing the material from 0 to  $\frac{3}{1000}$  in. depth from the surface. He found absolutely no difference between the patterns produced from these various sections. If, then, there is a surface effect, it must be much nearer the surface than this.

We have under way, at the present time, some experiments using radiation of a much less penetrating nature and are making the diffraction patterns from practically the surface of the sample, which we hope will throw some more light on this very interesting problem.

E. A. CAPILLON, Attleboro, Mass. (written discussion).—The authors of this paper are to be complimented on the illuminating comparisons which they draw

between cold-rolling of sheet, drawing of wire and corresponding conditions in tube drawing. I should like to obtain the authors' opinion on the conditions that exist when a tube is drawn so as to reduce only the circumference. No mandril being used inside the tube, the wall actually increases in thickness, the amount of this increase depending on total reduction in diameter and on the physical properties of the metal or alloy being drawn. It is well known that under these conditions tubes made of certain nonferrous alloys will almost invariably crack longitudinally on annealing, this failure being termed "fire cracking." In drawing gold-alloy tubes this is very apt to occur with the harder alloys, such as white golds of the Au-Cu-Zn-Ni type. I should be interested to know how the crystals are oriented in this case. Apparently a condition of high internal stress exists which is relieved by cracking of the material at elevated temperatures.

J. T. NORTON (written discussion).—In reply to the question of Mr. Capillon regarding the structure of tubing which has been reduced in such a fashion as to increase the wall thickness, no experimental evidence is available. If this type of reduction is carried very far, the deformation will not be symmetrical and the inside will be in quite a different condition from the outside. In general, however, I believe that the orientation will be essentially the wire structure. There are unquestionably very considerable stresses in tubes drawn in this way, and the alloys which crack on annealing are probably those of which the strengths decrease rapidly with increasing temperature, so that they rupture before the strains can be relieved by the beginning of recrystallization.

# Studies upon the Widmanstätten Structure, III.—The Aluminum-rich Alloys of Aluminum with Copper, and of Aluminum with Magnesium and Silicon\*

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(New York Meeting, February, 1932)

THE solid solutions which aluminum forms with copper, and with magnesium and silicon, are not extensive, and accordingly could not be expected to form Widmanstätten figures profusely nor with great ease. A study of the Widmanstätten figures in these systems seemed desirable, however, because of the interest which these alloys bear towards age-hardening theories resulting from the necessary relationship between the age-hardening phenomena and the atomic processes leading to the formation of Widmanstätten figures.<sup>1</sup>

## ALLOYS OF ALUMINUM WITH COPPER

The most accurate determination of the solid solubility of copper in aluminum seems to be that by Dix and Richardson,<sup>2</sup> whose results are represented in Fig. 1. According to this work, aluminum dissolves 5.6 weight per cent of copper at 548°, and less than one per cent at room temperature. Judging from the constitutional diagram, this solid solution on cooling tends to precipitate the compound  $\text{CuAl}_2$ , and this conclusion has been confirmed experimentally by Schmid and Wassermann.<sup>3</sup>

\* Published with the permission of the Navy Department, Washington, D. C.

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§ Naval Research Laboratory and Yale University.

<sup>1</sup> R. F. Mehl and C. S. Barrett: Studies upon the Widmanstätten Structure, I.—Introduction. The Aluminum-silver and Copper-silicon Systems. *Trans. A. I. M. E., Inst. Metals Div.* (1930) 78; R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structure, II.—The Copper-zinc and the Copper-aluminum Alloys. *Idem*, 123.

<sup>2</sup> E. H. Dix, Jr. and H. H. Richardson: Equilibrium Relations in Aluminum-copper Alloys of High Purity. *Trans. A. I. M. E.* (1926) 73, 560–580.

<sup>3</sup> E. Schmid and G. Wassermann: Studies upon the Duralumin Problem. *Metallwirtschaft* (1928) 7, 1334–1335.

Some suggestions of Widmanstätten figures may be found in several publications; Dix and Richardson, in the paper just mentioned, published a photomicrograph of an alloy with 1.6 weight per cent copper (Fig. 4b), showing a Widmanstätten figure exhibiting only three directions of

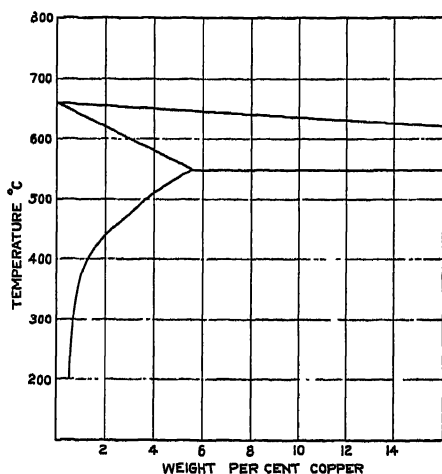


FIG. 1.—CONSTITUTION OF ALUMINUM-RICH ALUMINUM-COPPER ALLOYS ACCORDING TO DIX AND RICHARDSON.

traces of plates on a surface of polish, and also one with 4.05 weight per cent copper showing a complex structure (Fig. 5c).

#### *Formation and Outward Form of Precipitate*

Seven alloys were prepared from high-purity aluminum (99.95 per cent Al), and a master alloy with 53 weight per cent copper prepared from high-purity aluminum and high-purity copper prepared by Hilger for spectroscopic purposes (with more than 99.9 weight per cent copper). The compositions of these alloys are shown in Table 1.

These alloys were prepared in lots of 200 g. by melting the aluminum in a graphite crucible in a high-frequency induction furnace and adding a predetermined weight of the master alloy. The molten alloy, after stirring and thorough skimming, was cast into an open horizontal iron ingot mold, previously coated with lime, giving an ingot approximately

TABLE 1.—*Compositions of Aluminum-copper Alloys*

Cu, Per Cent	Fe, Per Cent	Si, Per Cent
1.12	0.05	0.036
1.63		
2.09		
3.11		
4.12		
5.02		
6.09		

$\frac{3}{4}$  by 1 by 5 in., which was quenched in water immediately after solidification. In order thoroughly to homogenize the alloys, and also to produce a large grain size, each ingot was given the following sequence of operations: (1) heated at 425° for 16 hr. (2) forged hot upon a power hammer to give a 50 per cent reduction in thickness; (3) imperfections ground off surface of billet; (4) heated to 425° for 1 hr.; (5) quenched in

water; (6) cold-rolled to give a 70 per cent reduction in thickness; (7) sound portion cut out of elongated billet in strip form; (8) heated at  $530^{\circ}$  for 40 hr.; (9) cooled in furnace from this temperature over a period of 3 hr.; (10) strip elongated in tensile machine 2 per cent; (11) heated at temperature of  $450^{\circ}$ , increasing to  $540^{\circ}$  over a period of five days; (12) quenched in water from  $540^{\circ}$ . This treatment gave a thoroughly homogenized alloy, with very large grains occasionally over 1 in. long.

In order to precipitate the  $\text{CuAl}_2$  in a form suitable for study, pieces were cut from the finished strip averaging  $\frac{1}{8}$  by 1 by  $\frac{1}{2}$  in. and given a precipitation heat treatment. Although many types of heat treatment were tried, none was found that gave a well-defined Widmanstätten figure for high copper concentrations, though satisfactory structures were obtained in the low-copper alloys. The heat treatment adopted consisted in a heating of the quenched pieces to  $250^{\circ}$  for one week, followed by a treatment at  $300^{\circ}$  for a second week. It was found that high temperatures gave a coarse and irregular structure, whereas low temperatures gave too fine a structure—the combination of a treatment at a low temperature followed by one at a somewhat higher temperature was found to be fairly satisfactory.

It has been apparent from earlier work, especially that of Dix and Richardson, that the  $\text{CuAl}_2$  precipitate takes the form of plates. Although the precipitate in these alloys has usually been described as "needles," the present work may serve to remove all doubt of the plate-like form of the precipitated particles, at least in the low-copper alloys. The types of structure found are shown in Figs. 2 to 5.

### *Determination of Plane of Precipitation*

All of the seven alloys listed in Table 1 have been studied, but on only three of these—the 1, 3, and 6 per cent alloys—have complete determinations of the plane of precipitation been attempted. These complete determinations consisted in the determination of the orientation of the solid solution matrix by X-rays, and a comparison of the derived directions of the traces of various crystallographic planes upon the surface of polish with the directions of the "needles" upon the surface of polish. Only a count of the number of directions of the "needles" was made for the alloys with  $1\frac{1}{2}$ , 2, 4 and 5 per cent Cu, but taken in connection with the complete analyses on the three alloys mentioned this simple count is sufficient to the purpose.

The etching agent used here was 0.5 per cent hydrofluoric acid in water, applied for 5 to 10 sec. The etching reaction of the particles found was so indefinite, because of the minuteness of the particles, that it could not be used to identify the phase. Since, however, Schmid and Wassermann have found  $\text{CuAl}_2$  in over-aged alloys with 4.5 per cent Cu,

and since in the present work diffraction lines correspond in position to those from  $\text{CuAl}_2$ , we may consider the precipitate observed to have been  $\text{CuAl}_2$ .

The types of structure studied are shown in Figs. 2 to 5. Figs. 2 and 5 are of grains analyzed crystallographically, whereas Figs. 3 and 4 represent other typical structures in this composition range. These photomicrographs show the precipitate to be chiefly in the form of plates, though occasionally—doubtless because of a spheroidizing action—indistinct small masses may be seen, as in Fig. 2. Furthermore, these

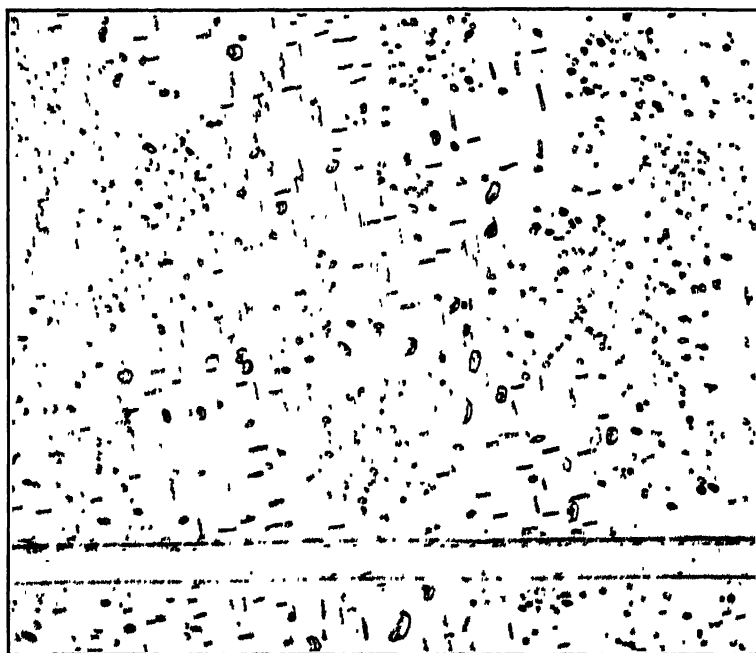


FIG. 2.—ALUMINUM-COPPER ALLOY, 1 PER CENT CU. ETCHED WITH 0.5 PER CENT HYDROFLUORIC ACID IN WATER.  $\times 750$ .

plates are well defined at low copper concentrations, but poorly defined at high, and, in particular, the number of directions shown by the intersections of the plates with the surface of polish—the plate traces—is small at low concentrations, but large at high concentrations. In Figs. 2 and 3 there is shown one family of plates lying nearly in the plane

FIG. 3.—ALUMINUM-COPPER ALLOY, 1 PER CENT CU. QUENCHED FROM  $548^{\circ}$  AND HEATED FIVE DAYS AT  $360^{\circ}$ . ETCHED WITH 0.5 PER CENT HYDROFLUORIC ACID IN WATER.  $\times 1000$ .

FIG. 4.—ALUMINUM-COPPER ALLOY, 1 PER CENT CU. QUENCHED FROM  $548^{\circ}$  AND HEATED FIVE DAYS AT  $350^{\circ}$ . ETCHED WITH 0.5 PER CENT HYDROFLUORIC ACID IN WATER.  $\times 1700$ .

FIG. 5.—ALUMINUM-COPPER ALLOY, 6 PER CENT CU. ETCHED WITH 0.5 PER CENT HYDROFLUORIC ACID IN WATER.  $\times 2000$ .



FIGS. 3-5.—CAPTIONS ON OPPOSITE PAGE



of polish, and two others the edges of which form approximately a right angle; the plates in the plane of polish are especially evident in Fig. 3. In Fig. 4, three directions are evident, with no plates in or nearly in the plane of polish. When one family of plates lay nearly in the plane of polish, it was observed that the outlines of these plates were usually square, parallel to the directions of the traces of the other two families of plates.

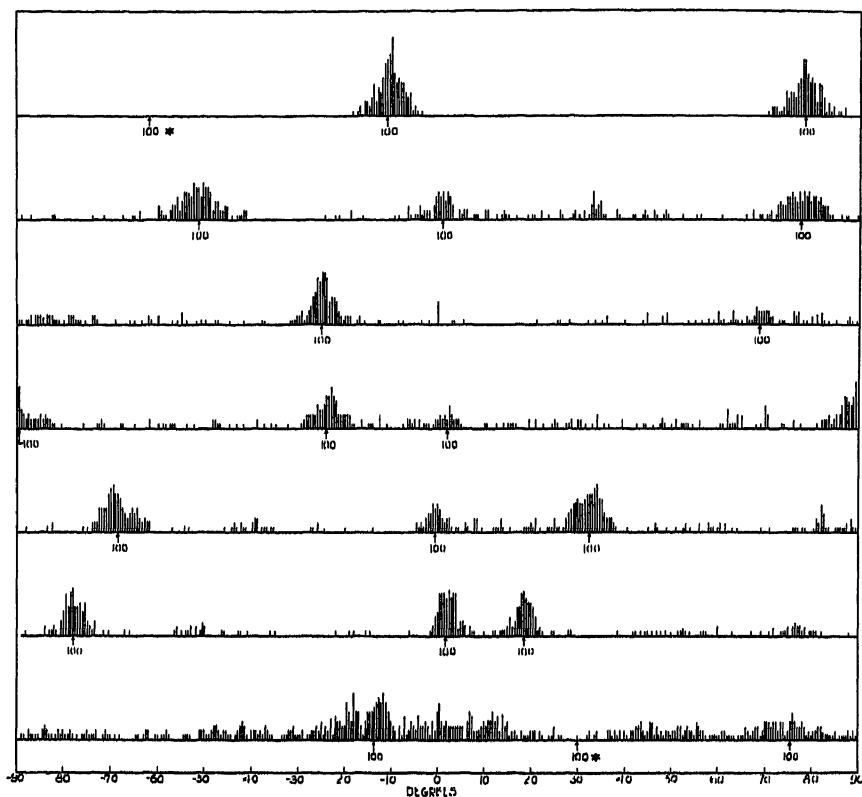


FIG. 6.—FREQUENCY CURVES FOR DIRECTIONS OF TRACES OF  $\text{CuAl}_2$  UPON PLANE OF POLISH IN ALUMINUM-COPPER ALLOYS.

Top line is frequency curve for 1 per cent Cu alloy, then in order follow curves for 1.5, 2, 3, 4, 5, 6 per cent Cu alloys. The shortest vertical line represents one trace in the indicated direction; the longer lines represent a greater number of traces in proportion to length. The small black stars indicate the presence of a family of plates lying nearly in the surface of polish and therefore not showing on the frequency curves.

The directions shown by the intersection of the plates by the plane of polish are shown by a frequency curve of the type used previously in this series of papers (Fig. 6). This was obtained as follows: a large grain was selected on a polished and slightly etched specimen, and a reference scratch drawn across the grain with a carefully pointed needle. A series of photomicrographs was taken, each to include the scratch, in order to determine the angles between the "needles" and the reference scratch.

Finally the angles made by a large number of "needles" with the reference line were measured on the photomicrograph. The photomicrographs were taken in groups of six, giving a large and continuous composite photomicrograph, affording a number of precipitate particles sufficiently large for the study of "needle" angles, and for the construction of a satisfactory frequency curve.

The top curve, from the 1 per cent Cu alloy (Fig. 2), shows two pronounced maxima, with a third not evident because of the fact that one set of plates lay in the surface of polish, and thus gave no measurable direction. Throughout this series of seven curves there are three prominent families of directions, a proof that the plates form on the (100) planes in the parent solid solution. But we note that besides these prominent maxima there are shown in the alloys from 1.5 to 6 per cent other directions to the traces; this is especially notable in the 6 per cent alloy, for which it is difficult to separate discrete maxima. The directions corresponding to the (100) planes, however, predominate throughout the concentration range of the solid solution.

Confirmation of the correctness of the assumption of the (100) plane as the plane of precipitation in the parent solid solution was obtained, as stated above, for the alloys with 1, 3 and 6 per cent Cu, by the use of X-rays. For this purpose, the selected grain was mounted in the X-ray camera used previously (Davey-Wilson) and the orientation of the selected grain with respect to the reference scratch and the plane of polish determined. These data were transferred directly to a stereographic projection, and the most likely angles of the "needle" families with respect to the reference scratch transferred from the frequency curve to the same projection and compared in position to the traces of the various crystallographic planes.

Of the three comparisons made, only one need be given here, that for the 3 per cent Cu alloy, for the other two yielded like results. In Fig. 6, the solid lines represent the directions of the traces of the plates on the surface of polish, as approximated from the frequency curve given in Fig. 6 (fourth from top), the dotted lines the direction of the traces of the (100) planes on the surface of polish of the grain, and the small circles the stereographic projections of the (100) planes (properly lying, in the projection, upon diameters at right angles to the directions of the respective planes).

The agreement in this plot (and in the other two) is satisfactory; not only are the plate traces parallel to the traces of the (100) planes on the surface of polish, but it was observed that the smaller the angle formed by the plate and the plane of polish, the less distinct the maximum on the distribution curve, and the less certain its angular position; until finally when broad plates were observed in the plane of polish (Fig. 2 and especially Fig. 3) only two maxima (at an angle of  $90^\circ$ )

appeared on the frequency curve instead of three, and the stereographic plot showed a (100) point very near the center of the large stereographic circle. All these facts are proof of the presence of plates of the  $\text{CuAl}_2$  on the (100) planes in the solid solution matrix.

There can be no doubt, therefore, that  $\text{CuAl}_2$  precipitates in the form of plates upon the (100) planes in the parent aluminum-rich solid solutions, yet not only in this manner, but also in some more obscure fashion, producing a wide scattering of directions on a polished surface. This complication is absent in low-copper alloys, but appears in the neighborhood of 1.5 per cent Cu, and increases to the 6 per cent alloy, where it is very severe. The difficulty of studying these fine particles discourages much attempt at an analysis of this more complicated precipitation. The frequency curve gives no help, for the additional precipitation appears there only as a fairly uniform background. Indeed, the indication of these other directions is so indistinct (Fig. 5) that it cannot be said whether the particles are in the form of plates or not. If truly platelike in nature, and if formed upon lattice planes in the aluminum-rich solid solution, they must form on some plane or planes of high index, with 12 or 24 members, giving many maxima the distinctness of which is lost owing to crudity of polish on the specimens studied and also to normal scattering from true position. At present this point must be left open.

#### *Further Experimental Studies*

The thesis has been maintained in these studies that the orientation of the lattice of the precipitate is of importance in determining the type of structure obtained. In general, this is hard to determine; in the present case very little success was obtained. The method offering the greatest promise of success was that used in the similar problem in the aluminum-silver system,<sup>4</sup> but a 65-hr. exposure on a drawn and heat-treated wire gave no results which could be interpreted, though some reflections from the  $\text{CuAl}_2$  lattice were noted; the difficulty doubtless arose from the very small amount of  $\text{CuAl}_2$  formed. Attempts to determine the orientation of the  $\text{CuAl}_2$  directly on the polished specimens by the use of the Davey-Wilson camera were hardly more satisfactory. The few lines obtained (on the stationary film) could be explained upon the assumption that the basal plane in the  $\text{CuAl}_2$  lattice was parallel to the (100) plane in the Al lattice, the distribution of the reflections showing a fourfold symmetry, consistent in the  $\text{CuAl}_2$  lattice only with the basal plane. Further, the angular position of the basal plane of the  $\text{CuAl}_2$  lattice upon the (100) plane in the aluminum lattice was, from the reflections obtained, *not* that represented by a parallelism of the two 100 directions in the two lattices.

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<sup>4</sup> R. F. Mehl and C. S. Barrett: Reference of footnote 1, 21-26.

These results are far from definite, and are given—hesitantly—because the only logical solution to the problem is one consistent with them. This we shall see later, in the discussion.

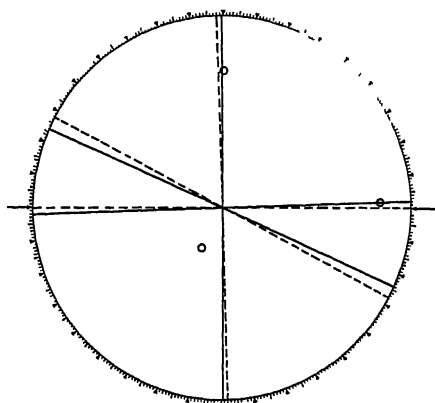


FIG. 7.—STEREOGRAPHIC PLOT FOR 3 PER CENT ALUMINUM-COPPER ALLOY, SHOWING TRACES OF  $\text{CuAl}_2$  PLATES IN SURFACE OF POLISH (SOLID LINES), TRACES OF (100) PLANES IN SURFACE OF POLISH (DOTTED LINES), AND POSITIONS IN SPACE OF (100) PLANES WITH RESPECT TO SURFACE OF POLISH (SMALL CIRCLES).

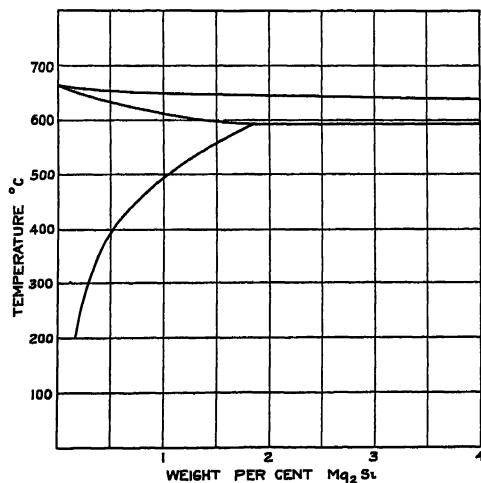


FIG. 8.—CONSTITUTION OF ALUMINUM-RICH ALUMINUM-MAGNESIUM-SILICON ALLOYS ACCORDING TO DIX, KELLER AND GRAHAM.

#### ALLOYS OF ALUMINUM WITH MAGNESIUM AND SILICON

Determinations of the solid solubility of  $\text{Mg}_2\text{Si}$  in aluminum have been attempted by Hanson and Gaylor<sup>5</sup> and by Dix, Keller, and Graham.<sup>6</sup>

<sup>5</sup> D. Hanson and M. L. V. Gaylor: Constitution and Age-Hardening of the Alloys of Aluminum with Magnesium and Silicon. *Jnl. Inst. Metals* (1921) **26**, 321-359.

<sup>6</sup> E. H. Dix, Jr., F. Keller and L. W. Graham: Equilibrium Relations in Al- $\text{Mg}_2\text{Si}$  Alloys of High Purity. *Trans. A. I. M. E., Inst. Metals Div.* (1931) 404.

The constitutional diagram derived by the latter workers is reproduced in Fig. 8. It is interesting to note that Dix, Keller and Graham observed a structure, obviously a Widmanstätten figure, exhibiting two directions of precipitate traces on the surface of polish (Fig. 6 in the paper by Dix et al.).

#### *Formation and Outward Form of Precipitate*

The alloys were prepared in a clay-graphite crucible. An aluminum alloy with magnesium and silicon was first prepared by adding magnesium to a 13 per cent silicon alloy to give a composition of 20 per cent  $Mg_2Si$ . The aluminum-magnesium-silicon alloys were formed by adding proper amounts of this master alloy to pure aluminum.<sup>7</sup>

Five of the six specimens were in the form of a composite specimen, bolted together in one holder, the sixth in the form of a thin strip. The analyses of the finished alloys were determined as shown in Table 2.

TABLE 2.—*Composition of Aluminum-magnesium-silicon Alloys*

Intended $Mg_2Si$ Composition, Per Cent	Mg, Per Cent	Si, Per Cent
1.00	0.67	0.36
1.25	0.82	0.46
1.50	0.98	0.55
1.75	1.16	0.62
2.00	1.21	0.76

The composite block of five pieces contained pieces of these five analyses. The sixth separate piece was fabricated from the same piece as the last in the table. No analyses for elements other than magnesium and silicon were carried out on the finished alloys. The purity of the finished alloys in this respect may be appraised from the analyses of the stock metals from which the alloys were made, which were as follows:

Metal	Si, Per Cent	Fe, Per Cent	Cu, Per Cent	Mn, Per Cent	Ti, Per Cent	Al, Per Cent
Al.....	0.007	0.009	0.016	nil	0.002	
Si.....		0.66	nil	0.04	0.10	0.56
Mg.....	nil	nil				0.01

The magnesium used also contained about 0.01 per cent of Group II metals.

The heat treatment of the composite alloy block consisted in a heating at 580° for 48 hr., a quench in cold water and a reheating to 350° for 24

<sup>7</sup> All these alloys were prepared by E. H. Dix, Jr., and kindly lent to the authors for the present study; in addition, most of the heat treatments were performed by Mr. Dix, and all the analyses were furnished by him.

hr. The separate strip ("2 per cent  $\text{Mg}_2\text{Si}$ ") was heated to  $540^\circ$ , quenched in water, cold-rolled 3 to 5 per cent, and reheated to  $540^\circ$  for 1 hr., in order to produce a large grain in the aluminum-rich matrix. The latter failing, the sheet was elongated 1.5 per cent, heated to  $540^\circ$  for 1 hr., air-quenched (air blast) and reheated at  $300^\circ$  for 48 hr., resulting

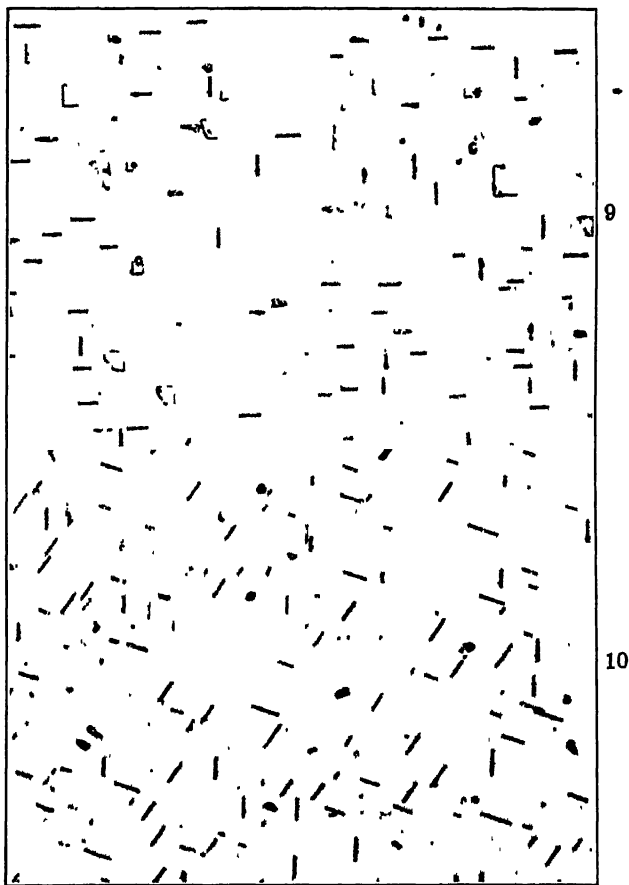


FIG. 9.—ALUMINUM-MAGNESIUM-SILICON ALLOY, "1.75 PER CENT  $\text{Mg}_2\text{Si}$ ." ETCHED WITH 0.5 PER CENT HYDROFLUORIC ACID IN WATER.  $\times 750$ .

FIG. 10.—ALUMINUM-MAGNESIUM-SILICON ALLOY, "1.75 PER CENT  $\text{Mg}_2\text{Si}$ ." ETCHED WITH 0.5 PER CENT HYDROFLUORIC ACID IN WATER.  $\times 750$ .

in a suitable precipitate structure and in a suitable large grain in the solid solution matrix.

The appearance of the precipitate upon the surface of polish, Figs. 9, 10 and 13, left no doubt that the precipitate took the form of true plates, and in addition showed that the plate edges were square, lying parallel to the plates on other planes. The formation of plates is also evident from the photomicrograph given by Dix, Keller and Graham.

*Determination of Plane of Precipitation*

Only one alloy was completely analyzed, the separate "2 per cent  $\text{Mg}_2\text{Si}$ " strip. This alloy was analyzed for the number of directions of plate intersections on the surface of polish, first by a simple count and second by a comparison with the directions of traces of the true crystallographic planes as determined by an X-ray analysis of the orientation of the matrix

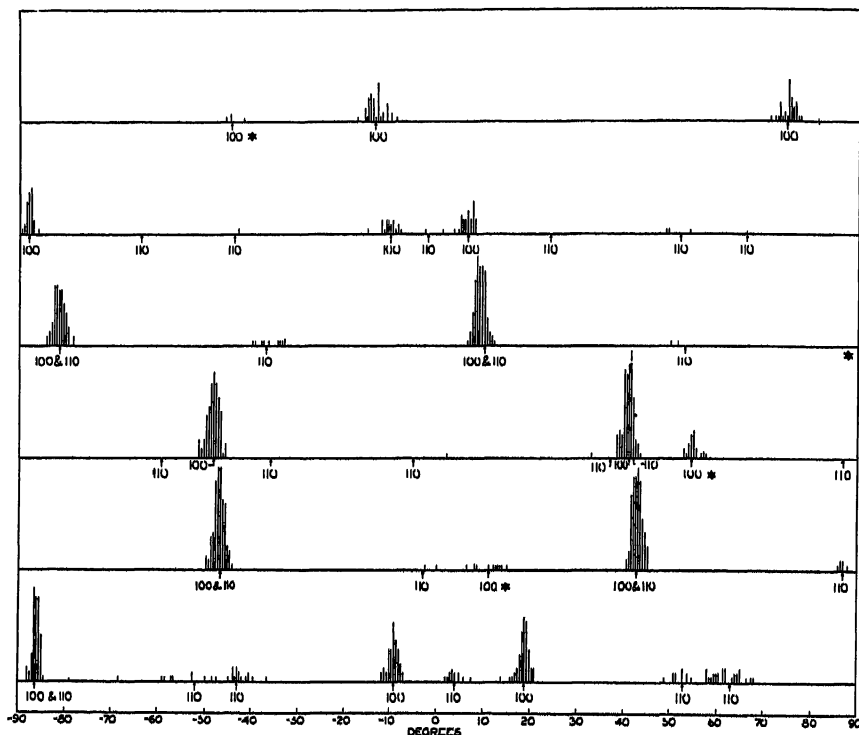


FIG. 11.—FREQUENCY CURVE FOR DIRECTIONS OF TRACES OF PRECIPITATE PLATES IN ALUMINUM-MAGNESIUM-SILICON ALLOYS UPON PLANE OF POLISH.

Top line is frequency curve for 2 per cent (sheet specimen), then in order follow curves for the alloys in "composite block" 1, 1.25, 1.50, 1.75, and 2 per cent " $\text{Mg}_2\text{Si}$ " alloys. The shortest vertical line represents one trace in the indicated direction; the longer lines represent a greater number of traces in proportion to length. The small black stars indicate the presence of a family of plates lying nearly in the surface of polish and therefore not showing on the frequency curve.

and the observed traces of the plate edges. The five alloys in the composite block, however, were studied only by means of a direction count.

The types of structures obtained are well represented by Figs. 9 and 10, both from the "1.75 per cent  $\text{Mg}_2\text{Si}$ " alloy. The other alloy compositions showed nearly identical structures, varying only in the amount of precipitate, as to be expected. The directions counted on these five compositions are listed in the frequency curves in Fig. 11.

It may be seen in this figure that in all the alloys there are three prominent directions, three well-defined maxima, but it may also be observed that there are some directions not accounted for by the three chief maxima, particularly in the bottom curve in Fig. 11. These extra directions, increasing in number with the content of magnesium and silicon, are never numerous, but nevertheless appear to be real. The three pronounced maxima suggest that the precipitate forms on the (100) plane in the aluminum-rich solid solutions, and this has been directly confirmed by X-ray determination of the positions of the (100) planes in the solid solution matrix. On this basis, the remaining directions—those

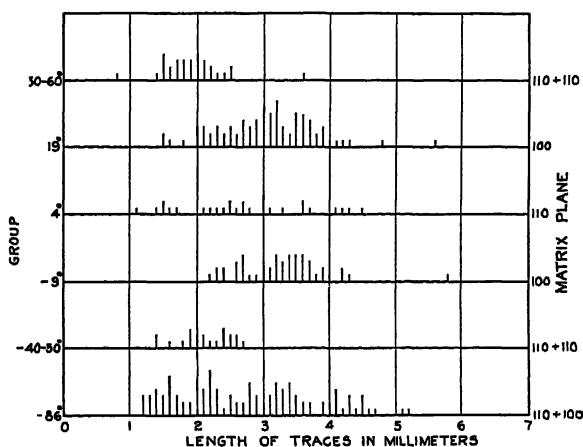


FIG. 12.—PLOT SHOWING LENGTHS OF TRACES OF PLATES INDICATED ON THE HORIZONTAL AXIS.

As measured from photomicrographs at 750 dia., and the number of traces of the plotted lengths, indicated by the lengths of the vertical lines, versus the angles upon the plane of polish at which each of the six groups represented obtained.

in addition to the three maxima—may be accounted for, at least with fair satisfaction, by the (110) planes, as shown in Fig. 11, where the angular positions of the (110) traces have been derived stereographically.

It was observed in studying the precipitated plates that the (100) traces appeared to be uniformly long and thin, whereas the (110) traces appeared to be shorter and somewhat thicker. In order to study this behavior, a plot of the lengths of the traces on the two planes was made, shown in Fig. 12. This diagram shows the lengths of the traces occurring in the maxima on the frequency curve (Fig. 11) at the angles designated on the ordinate axis: the lengths of the traces are shown on the horizontal axis and the number of traces of each represented length is shown by the relative heights of the vertical lines where the shortest line represents one trace. It may be seen from this diagram that the lengths of the plate edges on the (100) planes are generally somewhat greater than those on the (110) planes. No attempt was made to compare the thicknesses of the plates.



The direct determination of the plane of precipitation was, as stated, performed upon the separate strip sample, "2 per cent  $\text{Mg}_2\text{Si}$ ." This alloy was first etched to reveal grain boundaries, and several of the grains were

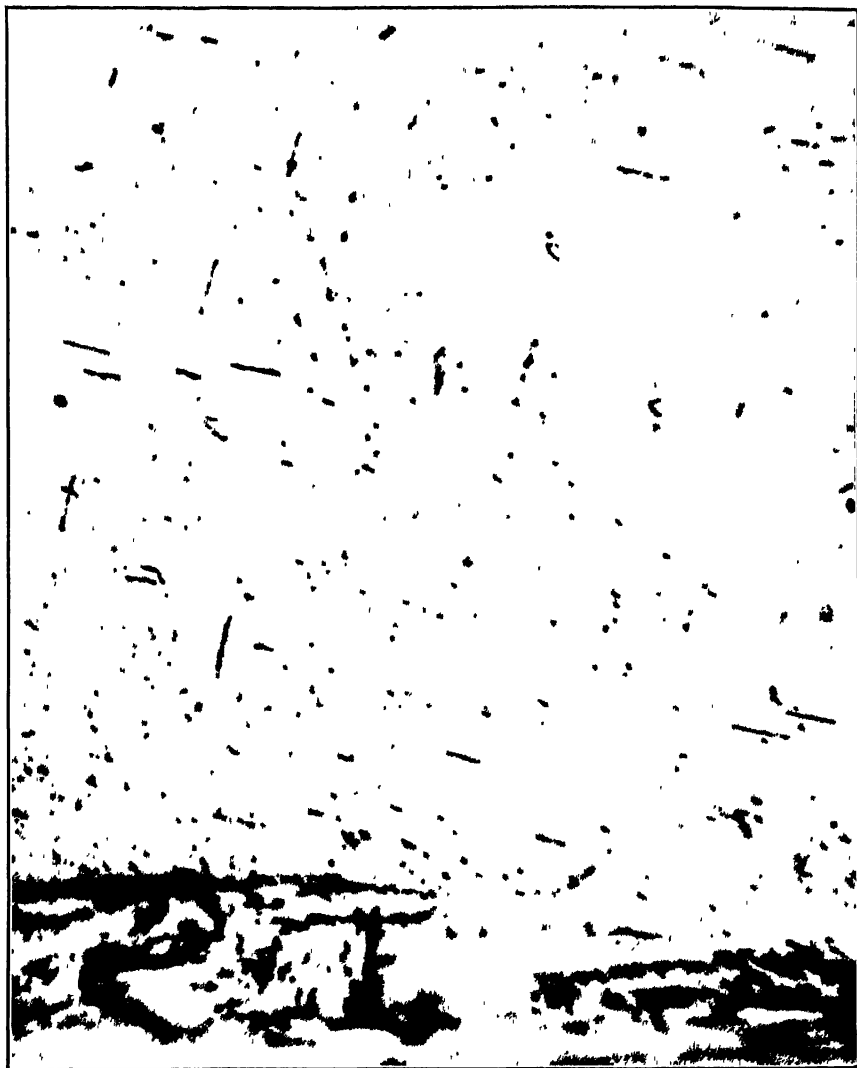


FIG. 13.—ALUMINUM-MAGNESIUM-SILICON ALLOY, "2 PER CENT  $\text{Mg}_2\text{Si}$ , SINGLE SHEET SPECIMEN." ETCHED WITH 0.5 PER CENT HYDROFLUORIC ACID IN WATER.  $\times 3000$ .  
Reduced one-third. Original magnification given.

then outlined by scratching with a needle. The specimen was then polished carefully, and etched with 0.5 per cent hydrofluoric acid in water.

One of the grains outlined was selected for the study of orientation. A line was drawn across it with a needle to serve as the reference line,

and a series of photomicrographs (3000 dia.) taken of adjacent sections, including in each case a portion of the reference scratch. In the grain studied, two sets of traces were found (Fig. 13), and the average angular portions of these directions with respect to the reference scratch determined by a frequency curve in the usual way.

This grain was then set up in the X-ray camera used previously, and the orientation of the lattice of the aluminum-rich solid solution matrix with respect to the surface of polish and the reference scratch determined. These X-ray data transferred to a stereographic projection gave the dotted lines and small circles in Fig. 14, representing, respectively, the traces of the (100) planes on the surface of polish and the stereographic projections of the (100) planes. The measurements of angles on the photomicrographs transferred to this projection (the solid lines) gave satisfactory confirmation of the choice of the (100) plane as the plane of precipitation. The wide divergence of one pair of these lines is clearly to be ascribed to the fact that the (100) plane concerned lay near the surface of polish, as shown by the stereographic point near the center of the great circle, giving a poorly defined plate edge on the polished surface.

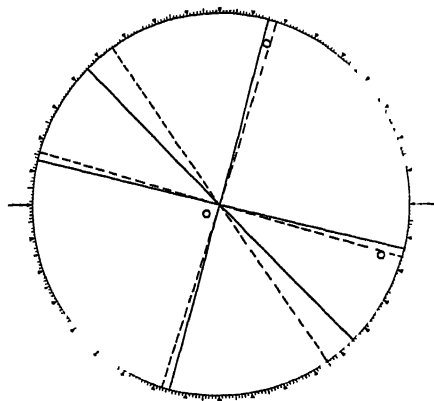


FIG. 14.—STEREOGRAPHIC PLOT OF "2 PER CENT  $Mg_2Si$ , SINGLE SHEET SPECIMEN," ALUMINUM-MAGNESIUM-SILICON ALLOY, SHOWING TRACES OF PRECIPITATE PLATES IN AL-MG-SI ALLOYS IN SURFACE OF POLISH (SOLID LINES), TRACES OF (100) PLANES IN SURFACE OF POLISH (DOTTED LINES), AND POSITIONS IN SPACE OF (100) PLANES WITH RESPECT TO SURFACE OF POLISH (SMALL CIRCLES).

It is clear, therefore, that the precipitate in these alloys is in plates chiefly upon the (100) planes, but the evidence for some precipitation upon the (110) planes seems incontrovertible.

### *Identity of the Precipitate*

It is generally assumed that the precipitate from this solid solution is  $Mg_2Si$ , and such was the assumption of the authors at the beginning of the present work. Attempts to demonstrate the presence of the  $Mg_2Si$  lattice, known from the work of Owen and Preston<sup>8</sup> were, however, unsuccessful in the instance reported.<sup>9</sup>

<sup>8</sup> E. A. Owen and G. D. Preston: The Atomic Structure of Two Intermetallic Compounds. Phys. Soc. (London) (1923-1924) 36, 341-348.

<sup>9</sup> E. Schmid and G. Wassermann: X-ray Studies on the Duralumin Problem. *Naturwissenschaften* (1926) 14, 980.

In the first specimen examined in this work, it was noted that where a large section of a precipitate plate was exposed to view (a plate lying nearly in the plane of polish), its etching reaction with the hydrofluoric acid gave a watery white color, rather than the bright blue to be expected of  $\text{Mg}_2\text{Si}$  with this etching agent. The same result was obtained in numerous cases where plate edges were revealed upon the surface of polish, and appeared to be the case for the precipitate on both the (100) and (110) planes. Although it might be supposed that the etching reaction of a phase in such a form could well be different from that for a primary phase—formed directly from the melt—it is disturbing not to be able to develop the characteristic etch. Although it may be held that the etching reaction should be dependent upon physical form and state of subdivision, it is hard to see why well exposed plates, such as those in Fig. 7, should not develop characteristic etch colors. Furthermore, finely divided primary  $\text{Mg}_2\text{Si}$  was found to give the characteristic etching reaction.

This result presented for study the question of the true identity of the precipitate phase. In order to obtain as direct evidence as possible, X-ray powder photograms were prepared of the alloys in the condition illustrated in the photomicrographs.

For this purpose, a portion of the separate strip sample ("2 per cent  $\text{Mg}_2\text{Si}$ ") was selected, powdered to pass a 250-mesh screen, mounted in a diffraction camera, and irradiated with the  $\text{Mo } K_\alpha$  and  $K_\beta$  radiation. The first sample chosen contained some primary  $\text{Mg}_2\text{Si}$  visible at the grain boundaries, not well adapted to the intended purpose; the results from this specimen were similar to those given in Table 3, obtained from a specimen with only a trace of primary  $\text{Mg}_2\text{Si}$ . Since the amount of precipitate was so small, an unusually long exposure time, 75 hr., was required, resulting in considerable general blackening of the film. The precipitate lines were all faint, and some listed below rather uncertain, though care was taken to have these lines confirmed independently by other observers.

Naturally the photograms showed all the aluminum lines. Since these aluminum lines sometimes occur where lines from precipitate should be, it is thought advisable to list all observed lines for comparison with the known spectra of the several possible phases.

Table 3 lists the diffraction lines found on the photogram, compared with the known lines<sup>10</sup>  $\text{Al}_3\text{Mg}_2$ ,  $\text{Mg}_2\text{Si}$ , and Si.

It is not easy to draw any very definite conclusions from these data, yet some analysis seems possible. Particular attention is drawn to the fact that the lines 1.493, 2.41 and 2.50 can be accounted for only by

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<sup>10</sup> We owe the spectrum for  $\text{Al}_3\text{Mg}_2$  to the kindness of Dr. Kent R. Van Horn, of the Aluminum Company of America. It was taken from a specimen containing 65 per cent Al and 35 per cent Mg.

TABLE 3.—*Diffraction Lines*

Experimental Value	Intensity <sup>a</sup>	Aluminum	Al <sub>3</sub> Mg <sub>2</sub>	Intensity <sup>a</sup>	Mg <sub>2</sub> Si	Intensity <sup>a</sup>	Si	Intensity <sup>a</sup>
1 010 <sup>a</sup>	V S	1 008 <sup>a</sup>						
1 044 <sup>a</sup>	V W						1 04 <sup>a</sup>	M
1 110 <sup>a</sup>	W						1 10 <sup>a</sup>	S
1 139 <sup>a</sup>	W	1 13 <sup>a</sup>						
1 170 <sup>a</sup>	V S	1 164 <sup>a</sup>						
1 195 <sup>d</sup>	V W							
1 220 <sup>a</sup>	V S	1 215 <sup>d</sup>						
1 250 <sup>a</sup>	M		1.242	W			1.24 <sup>a</sup>	M
			1.272	V W				
1 298 <sup>b</sup>	M	1.30 <sup>a</sup>	1 299 <sup>c</sup>	V W	1.292 <sup>c</sup>	S		
			1 324	V W				
			1 353	V W				
1 370 <sup>b</sup>	M	1 37 <sup>a</sup>	1 386 <sup>c</sup>	V W	1 37 <sup>a</sup>	V W		
1 400 <sup>d</sup>	V W				1 392	V W		
1 430 <sup>a</sup>	V S	1.429 <sup>a</sup>	1 425 <sup>c</sup>	S	1 42 <sup>a</sup>	V W		
					1.452	W		
1 493 <sup>a</sup>	V W		1 49 <sup>a</sup>	S	1 481	W		
1 544 <sup>b</sup>	VV W		1 53 <sup>b</sup>	V W	1 535 <sup>b</sup>	V W		
			1.57	W	1.582	M		
1 615 <sup>a</sup>	M	1 610 <sup>a</sup>						
1 643 <sup>b</sup>	V W		1 64 <sup>b</sup>	V W	1.638 <sup>b</sup>	V W	1.63 <sup>a</sup>	S
1 690 <sup>b</sup>	VV W		1.71 <sup>b</sup>	V W	1.68 <sup>b</sup>	V W		
1.760 <sup>d</sup>	W		1.78	V W	1.785	W		
1 85 <sup>b</sup>	V W		1.86 <sup>c</sup>	V W	1 85 <sup>b</sup>	W		
1.92 <sup>a</sup>	VV W		1 94	W	1.92 <sup>b</sup>	M	1.91 <sup>a</sup>	S
1.970 <sup>d</sup>	VV W							
2 025 <sup>a</sup>	V S	2 021 <sup>a</sup>	1.99 <sup>c</sup>	W	2 02 <sup>c</sup>	M		
2.13 <sup>a</sup>	VV W		2 12 <sup>a</sup>	M	2 11 <sup>b</sup>	W		
2 19 <sup>a</sup>	VV W		2 20 <sup>a</sup>	M				
2 25-2 30 <sup>a</sup>	M	2.274 <sup>a</sup>	2.26 <sup>b</sup>	V W	2 24 <sup>a</sup>	V S		
					2 28 <sup>a</sup>	W		
2.35 <sup>a</sup>	V S	2 331 <sup>a</sup>	2.32 <sup>a</sup>	M	2 34 <sup>a</sup>	W		
2 41 <sup>a</sup>	M		2.38 <sup>a</sup>	V S	2.42 <sup>b</sup>	W		
2.50 <sup>a</sup>	W		2.48 <sup>a</sup>	V S				
2 65 <sup>a</sup>	M	2 60 <sup>a</sup>	2.69 <sup>c</sup>	W				
2 80 <sup>b</sup>	VV W		2.82 <sup>b</sup>	W	2 81 <sup>b</sup>	M		
2.90 <sup>d</sup>	M				2 91	V W		
3 05 <sup>d</sup>	V W				2.98	V W		
3.20 <sup>a</sup>	W				3.12 <sup>b</sup>	M	3 10 <sup>a</sup>	S
					3.21 <sup>b</sup>	W		
3 30 <sup>d</sup>	W				3.40	W		
3 58 <sup>a</sup>	W				3 62 <sup>a</sup>	S		

<sup>a</sup> = line completely accounted for.<sup>b</sup> = two or more lines superimposed to account for one experimentally determined line.<sup>c</sup> = presence of lines masked by strong Al line.<sup>d</sup> = lines not completely accounted for<sup>e</sup> Symbols: V S, very strong; S, strong; M, medium; W, weak; V W, very weak; VV W, extremely weak.

the lines 1.49, 2.38 and 2.48 of Al<sub>3</sub>Mg<sub>2</sub>, all very strong lines in the Al<sub>3</sub>Mg<sub>2</sub> spectrum; since the 1.48 and 2.42 lines of Mg<sub>2</sub>Si are probably too weak to give the intensity noted for the 1.493 and 2.41 lines, and no line appears for Mg<sub>2</sub>Si or Si to account for the 2.48 line in the specimen. Several lines of the Mg<sub>2</sub>Si spectrum are missing (1.392, 1.452, 1.481, 1.582, 1.785, 2.91, 2.98, 3.40) as also from the Al<sub>3</sub>Mg<sub>2</sub> spectrum (1.242,

1.272, 1.353, 1.57, 1.78, 1.94), but these are all weak lines in the normal spectrum; their absence in the present spectrum is not surprising. Comparison with the silicon spectrum is more difficult, for silicon characteristically shows only a few lines; the lines at 1.044 and 1.110 seem suitably explained by the 1.04 and 1.10 lines in the silicon spectrum, but the apparent absence in the spectrum of the silicon lines 1.24, 1.63, and 3.10, all strong lines, throws some doubt upon the presence of silicon in the sample.

The best conclusion that can be drawn from these uncertain data is that  $\text{Al}_3\text{Mg}_2$  is probably present, and that  $\text{Mg}_2\text{Si}$  and Si may be absent.

With this result the etching characteristics of the precipitate were re-examined. It was found that the precipitates on the (100) planes and in the (110) planes etched in identical fashion, with both 0.5 per cent hydrofluoric acid in water and with 25 per cent nitric acid in water, and the conclusion seemed justified that the phases on these two planes are one and the same chemical entity. Furthermore, the etching characteristics of the precipitate plates, the development of a watery gray appearance on etching with 25 per cent nitric acid in water at 70° C., were identically those for  $\text{Al}_3\text{Mg}_2$ , as described by Dix and Keith;<sup>11</sup> the primary  $\text{Mg}_2\text{Si}$  etched typically as described by Dix and Keith. This was the most convincing of the etching tests.

If, then,  $\text{Al}_3\text{Mg}_2$  is present in the alloy, and if the phases represented on the two atom planes are identical, an alloy of aluminum and magnesium precipitating  $\text{Al}_3\text{Mg}_2$  on cooling should give precipitation in plates upon these two planes. In an endeavor to test this conclusion, an alloy with 8 per cent magnesium was prepared and heat-treated to form a Widmanstätten figure. The best figure was obtained with an "aging" treatment at 300° for one week following the solution heat treatment. This structure was not well defined; a crystallographic analysis on the poorly defined structure gave rather uncertain indication of precipitation in plates on both the (100) and the (110) planes.

It is difficult to submit this phase of the problem to any rigorous experimental technique. Admitting that the evidence is not conclusive, it appears justified to conclude that the compound  $\text{Al}_3\text{Mg}_2$  is present in the alloys examined, and that the presence of  $\text{Mg}_2\text{Si}$  and Si is less certain.

With this uncertainty in the nature of the precipitate, attempts to study crystallographic relationships between the lattice of the parent solid solution and that of the precipitate seemed nearly useless. It was found that  $\text{Mg}_2\text{Si}$  lattice showed no lattice planes similar in pattern

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<sup>11</sup> E. H. Dix, Jr. and W. D. Keith: The Etching Characteristics of Constituents in Commercial Aluminum Alloys. *Proc. Amer. Soc. Test. Mat.* (1926) **26**, Pt. 2, 317-334.

and parameter to lattice planes in the matrix, at least among low-index planes.<sup>12</sup>

The lack of knowledge of atom positions in the  $\text{Al}_3\text{Mg}_2$  lattice makes such a comparison impossible at present. A complete crystallographic analysis of the precipitation in these alloys cannot therefore, be attempted.

## DISCUSSION OF RESULTS

The alloys studied here present special difficulties to a complete analysis of the crystallographic process leading to the formation of the Widmanstätten figures, chiefly because of the small amount of precipitate which may be obtained. The results therefore do not throw as much light on the general problem of what might be called "the Widmanstätten mechanism" as those from alloys forming Widmanstätten figures more profusely.

One result, however, stands out prominently. The aluminum-rich solid solutions of aluminum with copper precipitates plates of  $\text{CuAl}_2$  which are parallel to the (100) plane in the solid solution lattice, and the aluminum-rich solid solution of aluminum with magnesium and silicon precipitates plates (of uncertain identity) which are parallel to the (100) and (110) planes. Remembering that the precipitate from the solid solution of silver in aluminum is in the form of plates upon the (111) plane in the lattice of the parent solid solution,<sup>13</sup> it is clear that the type of Widmanstätten figure formed from a common type of lattice with a common base metal may vary according to the nature of the precipitate.

The early results on aluminum-silver and copper-silicon alloys showed that solid solutions may have the same type of lattice (face-centered cubic in these two cases) and yet form precipitates in plates on lattice planes of different index,<sup>14</sup> and later results on the precipitation of the  $\alpha$  and  $\gamma$  phases from the  $\beta$  in the Cu-Zn system<sup>15</sup> showed a fundamental difference in the precipitation of two different lattices from one basic lattice; with these early results the present may be taken to remove the question from reasonable dispute. Whatever the true explanation of the formation of the Widmanstätten figures may be, it will necessarily

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<sup>12</sup> If the theoretical reasoning in this work be accepted, might it not be reasoned that the absence of similar lattice planes in the aluminum lattice and the  $\text{Mg}_2\text{Si}$  lattice would militate against the formation of the  $\text{Mg}_2\text{Si}$  lattice during precipitation?

It might also be argued that since the aging process is probably conditioned by the formation of nuclei of the composition of the precipitate, the formation of nuclei of  $\text{Mg}_2\text{Si}$  is governed by a low degree of probability, for this would require the simultaneous presence of both magnesium and silicon in the proportions  $\text{Mg}_2\text{Si}$  and the absence of aluminum atoms. Such a nuclei formation should be inherently less likely than the formation of nuclei containing aluminum atoms, provided, of course, that all other conditions were equal.

<sup>13</sup>, <sup>14</sup> R. F. Mehl and C. S. Barrett: Reference of footnote 1.

<sup>15</sup> R. F. Mehl and O. T. Marzke: Reference of footnote 1.

contain elements separate from those pertaining to the parent solid solution only, factors introduced by the specific properties of the precipitate.

Attempts to determine the orientation of the lattice of the precipitate with respect to the lattice of the parent solid solution were unsuccessful in the one attempt made. Although the nature of the precipitate may be confidently assumed in the aluminum-copper alloys, such is not the case in the alloys of aluminum-magnesium-silicon. On the other hand, the precipitate is clearly on the (100) planes and (110) planes, and these only, in the aluminum-magnesium-silicon alloys, whereas in the aluminum-copper alloys though low concentrations of copper lead a simple precipitation of (100) planes, higher lead to a complex precipitation difficult to study and analyze. Thus, each of the two alloys studied presents a major difficulty.

Whatever may be the true composition of the precipitate in aluminum-magnesium-silicon alloys, it is fairly certain that in these alloys one phase precipitates upon two planes in the lattice of the present solid solution. This, if true, is a new fact. If the selection of the plane for precipitation be determined by a matching of this plane with a plane in the precipitate, it is not impossible that in this case two such pairs of closely similar planes obtain, leading to the selection of two planes of precipitation in the solid solution matrix.

The complex type of precipitation in the aluminum-copper alloys is more difficult to explain. It is possible that the heat treatment to render all the precipitate in the higher copper concentrations clearly Widmanstätten in nature was not discovered. It is difficult to see why merely increasing copper concentration should lead to the selection of an additional plane of a very high index, giving a large number of plate traces in addition to those from the (100) planes.

The selection of the (100) plane for precipitation in the low-copper alloys, however, may be explained simply, for it may be shown that the  $\text{CuAl}_2$  lattice contains a plane of atoms very similar in pattern and interatomic distances to the (100) plane in the solid solution lattice.

The lattice structure of  $\text{CuAl}_2$  has been determined by Friauf.<sup>16</sup> It is tetragonal with  $a_0 = 6.04$ , and  $c_0 = 4.86$ , and with the coordinates of the copper atoms as follows:  $0, 0, 0; 0, 0, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, \frac{1}{2}, 0$ , and those of the aluminum atoms,  $u, \frac{1}{2} + u, \frac{1}{4}; \frac{1}{2} - u, u, \frac{1}{4}; u, \frac{1}{2} - u, \frac{1}{4}; \frac{1}{2} + u, u, \frac{1}{4}; \frac{1}{2} + u; u, \frac{3}{4}; u, \frac{1}{2} - u, \frac{3}{4}; \frac{1}{2} - u, u, \frac{3}{4}; u, \frac{1}{2} - u, \frac{3}{4}$  where  $u = 0.158$ . This structure is represented in Fig. 15. The aluminum atoms are distributed in two planes parallel to the  $XY$  plane at  $\frac{c_0}{4}$  and  $\frac{3c_0}{4}$ . Let us consider one of these planes, that at  $\frac{3c_0}{4}$ , in which the arrangement of atoms is that shown in Fig. 16 ("black atoms").

<sup>16</sup> J. B. Friauf: The Crystal Structure of Two Intermetallic Compounds. *Jnl. Amer. Chem. Soc.* (1927) **49**, 3107.

The arrangement of atoms on the (100) plane in the aluminum-rich solid solution may be considered as that of a simple cubic plane with the interatomic distance  $2.86\text{\AA}$ , as shown in Fig. 16 ("white atoms").<sup>17</sup>

These two patterns may be superimposed, as in Fig. 16, by bringing into coincidence two directions of the type [120] in the  $\text{CuAl}_2$  lattice with two of the type [110] in the aluminum solid solution lattice; the extensive matching of atom positions is clearly evident.

This matching has some interesting features. The four atoms  $A, B, D, C$ , on the aluminum lattice is seen to agree closely with the four atoms  $A', B', C', D'$  in the  $\text{CuAl}_2$  lattice. Looking farther, however, the

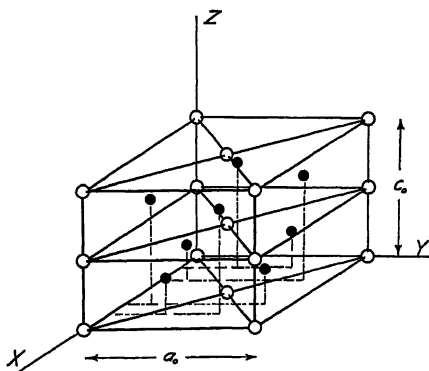


FIG. 15.

FIG. 15.—UNIT CELL OF  $\text{CuAl}_2$  ACCORDING TO FRIAUF. "WHITE ATOMS" ARE COPPER, AND "BLACK ATOMS" ARE ALUMINUM.

FIG. 16.—SUPERIMPOSITION OF THE (001) PLANE IN  $\text{CuAl}_2$  ("black atoms") AND THE (100) PLANE IN THE ALUMINUM-RICH ALUMINUM-COPPER SOLID SOLUTION ("WHITE ATOMS"), WITH TWO DIRECTIONS OF THE TYPE [120] IN THE  $\text{CuAl}_2$  LATTICE PARALLEL TO TWO DIRECTIONS OF THE TYPE [110] IN THE ALUMINUM-RICH SOLID SOLUTION LATTICE, AS REPRESENTED BY THE ARROWS. COPPER ATOMS ON THE NEXT LEVEL IN THE  $\text{CuAl}_2$  LATTICE ARE REPRESENTED BY THE SMALL CIRCLES WITH CROSSES.

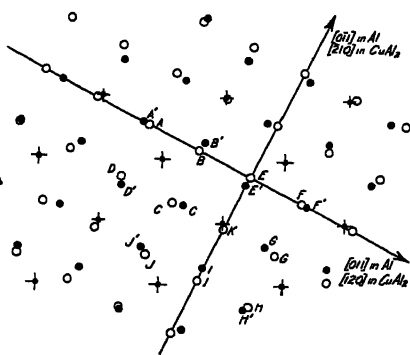


FIG. 16.

atom  $K$  on the aluminum lattice is seen to have no counterpart on the  $\text{CuAl}_2$  lattice, but as if intolerant of this vacancy, atoms  $E', G', I', C'$ , have taken positions nearer the vacant position. These features are repeated throughout the two planes, except that the matching of atoms becomes poorer as the distance from  $E$  (where the axes in the two planes were made coincidental) becomes greater owing to the greater spread of the atoms on the aluminum plane (linearly in the ratio  $2.86:2.70$ ).

The near identity in atom position of these two conjugate planes is in keeping with the general theory of the formation of Widmanstätten

<sup>17</sup> The variation in  $a_0$  for the face-centered cubic solid solution of copper in aluminum has been studied by Frhr. von Göler and G. Sachs: The Age-hardening of an Aluminum Alloy as Revealed by X-Ray Diffraction. *Metallwirtschaft* (1929) 8, 671-80. For pure aluminum a value of  $a_0 = 4.0402\text{\AA}$  was found, and for a 5 per cent Cu alloy a value of  $4.0300\text{\AA}$ . For the present purpose a general value, applying over the whole concentration range, of  $4.04\text{\AA}$  will be taken.



figures, for on this basis the (100) plane in the aluminum solid solution lattice could transform to the indicated (001) plane in the  $\text{CuAl}_2$  lattice with only a very slight shifting of atoms.

Although the attempts to determine the orientation of the precipitate lattice were largely unsuccessful, it should be pointed out that the indication of a fourfold axis normal to the (100) plane in the aluminum solid solution lattice is in keeping with the relationship in orientation postulated in Fig. 16. In view of the uncertainty in these results, probably the best that can be said is that proper conditions obtain in these alloys to give precipitation on the (100) plane in the aluminum solid solution by the type of mechanism previously postulated to explain Widmanstätten figures.

In view of the unusual metallurgical interest in these alloys, it may be permissible to inquire further into possible atomic movements. The (100) plane in the aluminum lattice doubtless contains both aluminum and copper atoms. With fluctuations in concentration, certain regions will show proper concentrations of the two atoms for precipitation, namely, one atom of copper to two atoms of aluminum. If it be true that the (100) plane in the aluminum lattice transforms into the (001) plane (at  $\frac{3c_0}{4}$ ) in the  $\text{CuAl}_2$  lattice,<sup>18</sup> the copper atoms must move away from the (100) plane in the aluminum lattice, since the indicated plane in the  $\text{CuAl}_2$  lattice contains no copper atoms. Fig. 16 shows that each vacant point in the  $\text{CuAl}_2$  plane of the type *K* corresponds to the presence of a copper atom just below (or above) it at a distance  $\frac{c_0}{4}$ , and that centered below (and above) each grouping of the type *A, B, C, D* there exists a copper atom at a distance  $\frac{c_0}{4}$ . It may be pictured that each copper atom at a point of the type *K* drops (or rises) to the next atom level, and in so doing draws in the atoms of the type *E', G', I', C'* towards the vacant point (and increases the normal interplanar distance, compare footnote above). On this basis, however, no explanation can be given for the movement of the copper atom centered below (or above) the groups of the type *ABCD*. It is possible that this atom takes its position by a simple diffusion process involving a shift of atoms from

<sup>18</sup> The above representation can also be shown for the two planes lying next to those in Fig. 16; indeed, the type of matching depicted in Fig. 16 is continuous throughout the two lattices. Thus, if we consider the aluminum lattice extended in the third dimension from the (100) plane in Fig. 16, and the  $\text{CuAl}_2$  lattice likewise extended, all atoms are in proper positions for the type of match shown in Fig. 16; i. e., no shearing of parallel atom planes is necessary. A considerable difference in interplanar spacing exists, however, for this is 2.02 Å in the aluminum lattice, but 2.43 Å in the  $\text{CuAl}_2$  lattice. This increase may be considered as conditioned by the intervening planes of copper atoms at  $\frac{c_0}{2}$ , etc.

lattice point to lattice point, and that the orientation of the lattice in the  $\text{CuAl}_2$  lattice is sufficiently determined by the extent of matching shown in Fig. 16. This relationship in orientation between the two lattices may be expressed as follows:

	AL LATTICE	$\text{CuAl}_2$ LATTICE
	(100) parallel to (001)	
	[110] parallel to [120]	
or equivalently	{	[100] parallel to [130]

Another matching of atomic planes is possible.<sup>19</sup>

If the conjugate planes shown in Fig. 16 are superimposed in such a way that the direction 110 in the aluminum lattice is parallel to the [100] direction in the  $\text{CuAl}_2$  lattice, a fair matching of atom positions obtains,<sup>20</sup> as shown in Fig. 17.

In this case the grouping  $ABCD$  transforms into the grouping  $A'B'C'D'$  by a small clockwise rotation; the group  $EFGH$ , lying immediately below it in the figure, transforms by a simple rotation of a few degrees and so on throughout the plane. With this transformation all the copper atoms normally lying on the (100) plane in the aluminum lattice would leave, taking their own level. The transformation could be represented as follows:

	AL LATTICE	$\text{CuAl}_2$ LATTICE
	(100) parallel to (001)	
	[110] parallel to [100]	
or equivalently	[100] parallel to [110]	

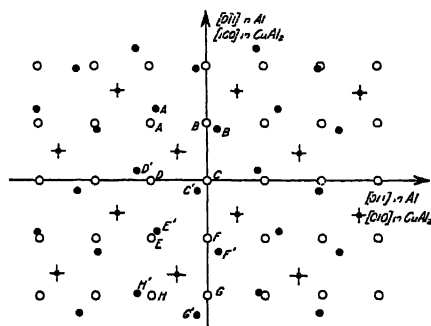


FIG. 17.—SUPERIMPOSITION OF THE (001) PLANE IN  $\text{CuAl}_2$  ("BLACK ATOMS") AND THE (100) PLANE IN THE ALUMINUM-RICH ALUMINUM-COPPER SOLID SOLUTION ("WHITE ATOMS"), WITH THE DIRECTIONS [100] AND [010] IN THE  $\text{CuAl}_2$  LATTICE PARALLEL TO TWO DIRECTIONS OF THE TYPE [110] IN THE ALUMINUM-RICH SOLID SOLUTION LATTICE, AS REPRESENTED BY THE ARROWS. COPPER ATOMS ON THE NEXT LEVEL IN THE  $\text{CuAl}_2$  LATTICE ARE REPRESENTED BY THE SMALL CIRCLES WITH CROSSES.

No decision can be made between these two mechanisms; since the first provides for an easier movement of the copper atoms, it may be considered the more likely. It might be pointed out here that in some of the photomicrographic specimens in which one of the three families of  $\text{CuAl}_2$  plates lay in the surface of polish, the outline of each plate was rectangular, the edge of the plate lying along the [100] direction in the aluminum lattice. This suggests that the orientation of the  $\text{CuAl}_2$  lattice is such that a prominent lattice direction lies parallel to the [100] direction in  $\text{CuAl}_2$ . The first solution proposed above would give this

<sup>19</sup> We are indebted to Mr. R. L. Davidson, of the Research Laboratories, The American Rolling Mill Co., for this suggestion.

<sup>20</sup> This is equivalent to a matching of a direction of the type [100] in aluminum and a direction of the type [110] in  $\text{CuAl}_2$ .

prominent direction to be of the type [130], whereas the second<sup>21</sup> would give [110].

Evidence is accumulating that there is a process obtaining in alloys of the duralumin type prior to actual precipitation causing much of the change in physical properties ordinarily described as "age-hardening." Recent work by Hengstenberg and Wassermann<sup>22</sup> suggests that this pre-precipitation process is most likely an agglomeration of copper atoms at numerous points within the aluminum solid solution. This pre-precipitation agglomeration might be represented in the following way: The fluctuations in concentration of the copper atoms (and aluminum atoms) within the aluminum-rich solid solutions lead to local concentrations equivalent to  $\text{CuAl}_2$ . At these points the aluminum solid solution lattice alters to conform to the  $\text{CuAl}_2$  lattice in the manner specified. The process of growth is slow, however, and these nuclei remain small. Because of the near-matching of the two lattices concerned, and because of the smallness of each nucleus, these nuclei do not separate from the aluminum solution matrix as a new phase, but remain as an integral part, causing lattice distortion as a result of imperfection in the match of the two lattices. As this nucleus grows, with the help of time or increased temperature, the registration of the two lattices becomes poorer and poorer, until, with the utter lack of registration, or when the resultant distortion becomes intolerable, the nucleus becomes a new phase, separated from the matrix phase by an interface or grain boundary.

The present study touches age-hardening theories at two other points. The age-hardening of duralumin at room temperature has for some years been attributed, at least in part, to  $\text{Mg}_2\text{Si}$ . Recent studies, however, seem to show that the presence of silicon is not necessary; presumably, therefore, the age-hardening at room temperature<sup>23</sup> is not caused by  $\text{Mg}_2\text{Si}$ . Although the problem is admittedly complex, it may be pointed out that the observations in the present study on the identity of the precipitate in aluminum-magnesium-silicon alloys offer

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<sup>21</sup> If we assume that the plate edge is bounded by a plane normal to the plane of polish (there was some indication of this) these planes will be, for the two cases discussed, (130) for the first and (110) for the second. The (130) plane has a high density of atoms if the aluminum atoms lying very slightly off the plane are considered in it (a density of 0.129 atoms per  $\text{\AA}^2$ ) whereas the (110) plane has a maximum density of atoms lying exactly on it of 0.0775 atoms per  $\text{\AA}^2$ ; atoms lying next to the (110) plane are considerably more distant than those lying next to the (130) plane.

<sup>22</sup> J. Hengstenberg and G. Wassermann: X-Ray Studies upon the Age-hardening of Duralumin at Ordinary Temperatures. *Ztsch. f. Metallkunde* (1931) 23, 114-117. This paper contains a list of the more important earlier papers upon this subject.

<sup>23</sup> The literature on this subject has recently been critically reviewed by K. L. Meissner. [The Artificial Ageing of Duralumin and Super-duralumin. *Jnl. Inst. Metals* (1930) 44, especially pages 223-227].

little support for the precipitation of  $\text{Mg}_2\text{Si}$  from them.<sup>24</sup> These observations, however, only incidental to the present work, require more definite proof.

It is interesting to note that the duplex character of the Widmanstätten figure obtained in aluminum-copper alloys appears to be reflected in the aging behavior of these alloys. Fraenkel<sup>25</sup> observed that an alloy with 4 per cent Cu, aged five days at room temperature, softened on first heating to 120° and then experienced a second hardening. It seems possible that the precipitation of  $\text{CuAl}_2$  upon the (100) plane may be the final result of one of these age-hardening processes, whereas the more complicated precipitation may represent the final result of the second process. Since the (100) precipitation should be the easier, because of its simple atom movements, it may be the manifestation of the room-temperature age-hardening process, and the more complicated precipitation that of the process operative at 120°.

#### SUMMARY

1. The Widmanstätten figures formed by precipitation from the aluminum-rich solid solutions in the systems aluminum-copper and aluminum-magnesium-silicon have been studied.

2. The precipitate of  $\text{CuAl}_2$  from the aluminum-rich solid solution in the aluminum-copper system takes the form of plates parallel to the (100) plane in the solid solution lattice throughout the solid solution range, and at concentrations greater than about 1.5 per cent Cu also in a form, probably platelike, bearing a more complicated (and undetermined) crystallographic relationship to the solid solution lattice.

3. The relationship in orientation between the lattice of the  $\text{CuAl}_2$  and that of the lattice of the solid solution matrix could not be determined; however, reasons are advanced to show that the (001) plane in  $\text{CuAl}_2$  should be parallel to the (100) plane in the solid solution, and the [110] direction in  $\text{CuAl}_2$  parallel to the [120] direction in the solid solution.

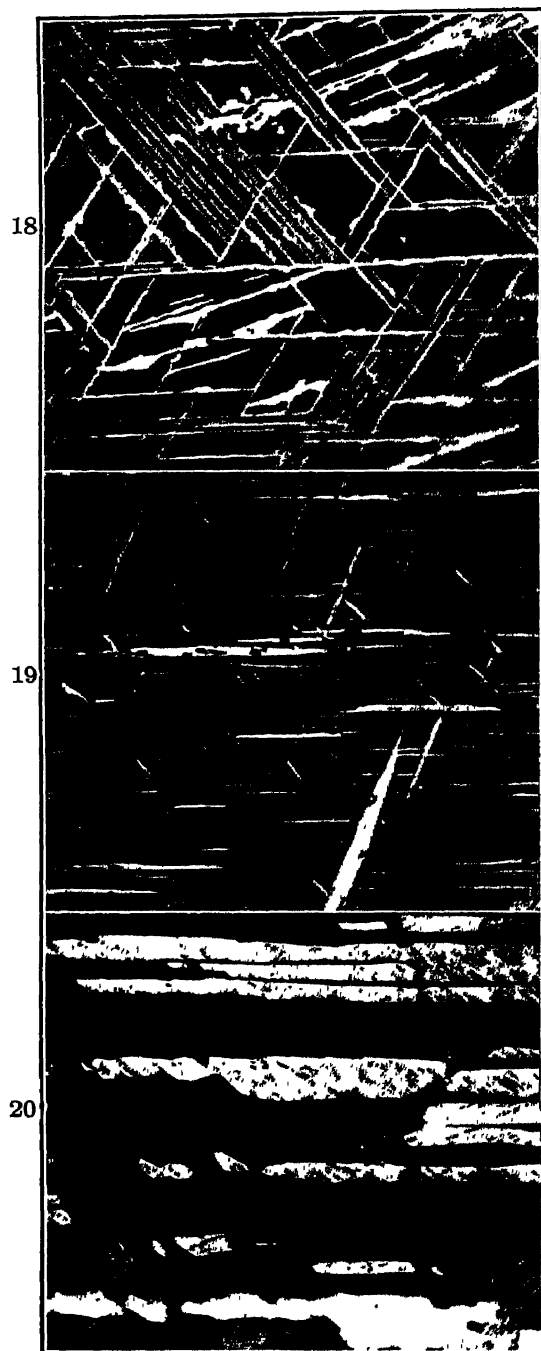
4. The precipitate from the aluminum-rich solid solution in the system aluminum-magnesium-silicon takes the form of plates, chiefly lying parallel to the (100) plane in the solid solution lattice, but also (at higher concentrations) of solute upon the (110) plane.

5. Attempts to demonstrate the chemical identity of this precipitate as that of  $\text{Mg}_2\text{Si}$  failed; etching tests and X-ray diffraction qualitative

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<sup>24</sup> It is strange that so little attention has been given to the possible effects of  $\text{Al}_2\text{Mg}_3$ , for though the solid solubility of magnesium in aluminum may be high at room temperature, the presence of silicon might well lower this solubility, as it appears to do in the alloys studied here.

<sup>25</sup> W. Fraenkel: Age-hardening Aluminum Alloys. *Ztsch. f. Metallkunde* (1930) 22, 84-89.



FIGS. 18-20.—CAPTIONS ON OPPOSITE PAGE.

analyses (and other tests) gave indications of the presence of  $\text{Al}_3\text{Mg}_2$ , but offered no support to the assumption of the presence of  $\text{Mg}_2\text{Si}$  or silicon.

6. The significance of these results to a general theory of the formation of Widmanstätten figures is pointed out; possible relationships to age-hardening theories are discussed.

## DISCUSSION

(*Arthur Phillips presiding*)

J. W. GREIG, E. POSNJAK and H. E. MERWIN, Washington, D. C. (written discussion).—In the series of papers of which this is the third the authors have first summarized what was known about the production of the Widmanstätten structure in metallic alloys, then reported on a series of well planned and skilfully executed experiments by which they have been able to sweep away a number of erroneous ideas, to add a very considerable body of carefully ascertained fact, and by their discussion to throw a good deal of light on the mutual crystallographic relationships of the members and on the mechanism of their separation. These papers are of great interest and fundamental importance not only to metallurgists but to all who are interested in crystals.

We have recently studied equilibrium between magnetite, hematite and oxygen over a limited temperature range.<sup>26</sup> In the neighborhood of  $1460^\circ\text{C}$ . solid solutions extend from  $\text{Fe}_3\text{O}_4$  to about  $75\text{Fe}_3\text{O}_4$ ,  $25\text{Fe}_2\text{O}_3$ , but the extent of solid solution decreases at lower temperatures. On cooling, or by reheating, the separation of hematite from the solid solution may be brought about, and a well developed structure results (Fig. 18). A strikingly similar result may be brought about by heating magnetite,  $\text{Fe}_3\text{O}_4$ , in air, in which case the oxygen to form the hematite comes from the air surrounding the crystal instead of from the solid solution (Figs. 19 and 20).

A number of mineralogists have studied hematite crystals growing on the faces of magnetite crystals and have completely determined the crystallographic relationship of the two species. Natural intergrowths of the two minerals due to partial

<sup>26</sup> Work to be published shortly.

FIG. 18.—GRAIN OF MAGNETITE-HEMATITE SOLID SOLUTION AFTER HAVING BEEN UNMIXED BY REHEATING.  $\times 750$ .

Solid solution made from  $\text{Fe}_3\text{O}_4$  by heating  $1\frac{1}{2}$  hr. in oxygen (1 atm.) at  $1460^\circ\text{C}$ ., then quenched by dropping into mercury under pure nitrogen. The solid solution, still a single phase, was sealed in an evacuated glass tube and heated at  $550^\circ\text{C}$ . This reheating brought about a separation into two phases. A typical grain is shown. Hematite, bright, forms lamellae parallel to the octahedral planes of the magnetite, gray.

FIG. 19.—MINEVILLE MAGNETITE (NO. 3B) PARTIALLY OXIDIZED IN AIR.  $\times 750$ .

Hematite, bright, forming lamellae in the magnetite, gray. As in the case illustrated in Fig. 18, the hematite lamellae are parallel to the octahedral planes of the magnetite crystal.

FIG. 20.—PARTIALLY OXIDIZED MINEVILLE MAGNETITE (NO. 3G), POLARIZED LIGHT.  $\times 400$ .

Nicols rotated from the crossed position. Three sets of hematite lamellae are shown. Their sections intersect at approximately  $60^\circ$ . The narrow darker lines cutting across the brighter hematite and the lighter lines cutting the darker hematite are lamellae of hematite twinned with respect to the main body of the hematite lamella. One set of hematite lamellae, because of their orientation with respect to the planes of the nicols, shows no twinning. The twinning of the hematite made it possible to determine completely the mutual orientation of the magnetite and hematite from a study of polished surfaces.

oxidation of the magnetite are also well known. We have been able to *completely* determine the crystallographic relationships of the two species in some of the coarsely-textured of our oxidation products. The relationship has been *incompletely* determined in the case of the intergrowths formed by ex-solution and there is little room for doubt that it is the same. The hematite lamellae are parallel to the octahedral planes of the magnetite. The hematite of a lamella is so oriented that its basal plane is parallel to that octahedral plane of the magnetite along which the lamella is deposited; further, the join of the plane of the base (0001) and of the unit rhombohedron (10 $\bar{1}$ 1) of the hematite is perpendicular to the join of that octahedral plane of the magnetite along which the lamella lies with another octahedral plane. This is the mutual orientation mineralogists have observed when hematite crystals occur on the faces of magnetite crystals.<sup>27</sup>

Royer<sup>28</sup> has recently extended the early experimental work of Barker on the deposition from solution of crystals of one species on the faces of a crystal of another species. He has applied the rules he formulated from that work to a number of naturally occurring examples, among them to the case of magnetite-hematite, and has shown that it is in agreement with them. In the common plane there is a close approach to equality in the spacing of certain iron atoms in the two structures, and nets formed by lines through these are parallel. Not all the iron atoms of these planes, but only certain ones, are at the nodes of these nets. As Royer puts it, "Il existe donc dans le plan commun une maille multiple qui a même forme et mêmes dimensions dans les deux espèces." A similar relationship, of course, exists between the arrangements of the oxygen atoms of the two species.

The generalizations arrived at by Royer on the requirements for mutual orientation are, we believe, in agreement with the data presented in these three papers on the Widmanstätten structure and, in their application to metals, would reduce to a rule similar to that set up by Mehl and Barrett in the first paper.<sup>29</sup> While they are by no means a sufficient basis for a complete explanation of the Widmanstätten structure, they do appear to be well established by a large body of data and to have sufficient bearing in this connection to warrant our drawing them to your attention.

It is interesting to note in naturally occurring magnetites<sup>30</sup> a further parallel with the behavior of alloys as shown by these studies. The plane of densest packing is not necessarily that along which the second phase separates, nor is the plane along which the second phase forms necessarily a cleavage plane.

G. DOAN, Bethlehem, Pa. (written discussion).—The authors suggest that the rounded particles of CuAl<sub>2</sub> may have formed by spheroidization during annealing; that is, by the predominance of surface tension over natural rigidity of the particles at the temperature of aging. This seems unlikely to occur in a substance as hard and rigid as CuAl<sub>2</sub> is at room temperature, due to such a slight elevation as 300° C. Possibly the circular sections are sections of needles, which may form as well as plates.

The identity of the "Mg<sub>2</sub>Si" precipitate is questioned by the authors. If the alloys obtained represent equilibrium, and if their composition actually falls on the line Al-Mg<sub>2</sub>Si, no other precipitate could be expected. The principle involved is that of Professor Guertler's "Klar Kreuz" method, which points out, briefly, that where two quasibinary systems are possible in a ternary diagram, as shown by the

<sup>27</sup> O. Mügge [*Neues Jahrb. Mineralogie*, etc., Beil. (1903) 16, 335–475] gives a summary of the literature on mutually oriented crystal growths.

<sup>28</sup> *Bull. Soc. Min. France* (1928) 51, 5–159.

<sup>29</sup> Reference to footnote 1, 108.

<sup>30</sup> For an illustrated description of a number of naturally occurring intergrowths, see Schneiderhöhn-Ramdohr: *Lehrbuch der Erzmikroskopie*, 2, Berlin, 1931.

dotted lines in Fig. 21, it is necessary only to prepare one alloy to decide the question as to which is the *real* system of two possible ones. The "clearing" alloy is the one at the intersection of the two dotted lines. If this alloy shows as its phases  $\text{Al}_3\text{Mg}_2$  and  $\text{Mg}$ , then the system  $\text{Al-Mg}_2\text{Si}$  is imaginary. In this case the system  $\text{Al-Mg}_2\text{Si}$  has been shown to be the real one and, therefore, *all* alloys on the line  $\text{Al-Mg}_2\text{Si}$  must, at equilibrium, exhibit these two phases and no others.

The third order reaction involving formation of  $\text{Mg}_2\text{Si}$  in an extensive solvent of aluminum would certainly be slow and probably incomplete, while that forming  $\text{Al}_3\text{Mg}_2$  could take place readily. The solubility of the latter (or of  $\text{Mg}$ ) in aluminum at the aging temperature is, however, quite high in the binary aluminum-magnesium system. If silicon atoms are so far away from the magnesium positions in the lattice, it would scarcely be wise to assume a decreased solubility of magnesium in aluminum due to these silicon atoms, or to expect the precipitation of the magnesium phase. I should prefer to consider, until condition to the contrary is proved, that  $\text{Mg}_2\text{Si}$  precipitates in all parts of this quasibinary system in the orthodox manner. The question is, however, an important one and not to be answered without experiment.

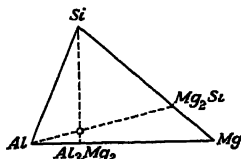


FIG. 21

R. F. MÆHL (written discussion).—The student of structure in metals and alloys owes much to the mineralogist and petrographer, for it should be remembered that Sorby, the pioneer in the microscopic examination of metals, was a petrographer. The petrographer and the metallographer are both concerned with crystals and both must study systems of several components, with changes in phase entirely similar in type; it is not surprising that the two sciences should have much in common and should be of mutual assistance. For this reason alone, it is pleasant to have the discussion by Messrs. Greig, Poznjak and Merwin.

It is interesting that the oxidation product of magnetite should show such a well defined Widmanstätten figure (Fig. 20). I am not certain whether the light-colored hematite lamellae were formed during the oxidation period or whether they formed in the usual way during subsequent cooling. The formation of nitride "needles"—a true Widmanstätten figure—resulting from nitrogen absorption in iron is somewhat similar in method of preparation to the formation of the hematite lamellae, though there can be no doubt that the nitride plates form during cooling and not directly during the nitriding process. I have recently found that Prof. J. W. Gruner,<sup>31</sup> of the University of Minnesota, has studied "oriented intergrowths" in minerals and has reached conclusions concerning the crystallographic mechanism similar in part to those expressed in this series of papers.

Dr. Barrett has mentioned the interesting relationship which Royer's work bears to the study of Widmanstätten figures.<sup>32</sup> Professor Menzies and Mr. Sloat, at Princeton University, have also studied crystal overgrowths,<sup>33</sup> extending the work of Royer; the overgrowth with mutual orientation obtained with  $\text{NH}_4\text{Br}$  and  $\text{CsCl}$  on silver is of particular interest to the metallurgist. Indeed, the whole question of orientation at interfaces should be considered as related to Widmanstätten figures, however indirectly—the oriented adsorption of hydrogen on platinum, the molecular orientation of oil

<sup>31</sup> J. W. Gruner: Structural Reasons for Oriented Intergrowths in Some Minerals. *Amer. Mineralogist* (1928) **14**, 227.

<sup>32</sup> See page 271.

<sup>33</sup> C. A. Sloat and A. W. C. Menzies: Phenomena Due to Forces at Crystal Faces as Studied by Mutual Orientations. *Jnl. of Phys. Chem.* (1931) **35**, 2005–2021; see also pages 2022–2025.



films on water. It seems probable that the tightly adhering film on corrosion-resisting metals owes its adherence and integrity to a molecular orientation similar to that of gases on metals and oil films on water.

The twins in the hematite lamellae which Messrs. Greig, Poznjak and Merwin mention can also be found in the Kamacite lamellae in meteorites. Why they form in either case is hard to say, and the question should be given some study.

It is quite true that this series of papers on the Widmanstätten structure has shown that the plane of precipitation of a plate need not be a cleavage plane, that indeed cleavage is in no way related to the factors determining the choice of plane. The usual designation of "precipitation on the cleavage planes" in fairness should be regarded, however, as a vestige of the older crystallographic nomenclature, devised when the only crystallographic planes known were the growth planes and those revealed by cleavage, and should therefore be taken as synonymous to the present-day terms "atom planes," or more simply "crystallographic planes."

F. N. RHINES (written discussion).—In the use of the term "spheroidizing action" (p. 206) it was not the intention of the authors to convey the idea of a reduction of the bounding surface of the precipitated particles by the forces of surface tension in just the manner of liquids, as Professor Doan seems to have understood. Rather, the mechanism of "spheroidization" was pictured principally as one in which the atoms of the precipitated crystal, in equilibrium with the solid solution matrix, were constantly being taken back into solution and redeposited elsewhere on the surface of the crystal, eventually resulting in a crystal form of minimum potential energy; that is, of spherical form. Ample proof of the existence of sufficient freedom of atom migration to allow of such a process may be had from the very fact that the precipitation of  $\text{CuAl}_2$  took place at the temperature of  $300^\circ\text{C}$ . used in the precipitation treatments. There is, of course, a possibility that the particles referred to are needlelike in form; however, since no elongated deposits grouped in the fashion of these rounded ones were observed, it seems probable that they are truly globular in form.

The second question which Professor Doan has raised is one that cannot be satisfactorily answered with the data now at hand. It may be of interest, nevertheless, to consider one explanation which is possibly, though by no means certainly, susceptible to experimental verification.

Since, as Professor Doan has pointed out, the phases  $\text{Mg}_2\text{Si}$  and  $\text{Mg}_2\text{Al}_3$  cannot co-exist in equilibrium in the range of composition of the alloys studied, and since, as we have been led to believe, both phases do appear at apparent equilibrium in the same alloy, we are inevitably forced to the conclusion that true equilibrium has not been attained in all cases. That is to say, either the  $\text{Mg}_2\text{Si}$ , which unquestionably forms at the grain boundaries in cast Al- $\text{Mg}_2\text{Si}$  alloys, or the supposed  $\text{Mg}_2\text{Al}_3$  which precipitates in the solid solution phase of such alloys cannot be present under conditions of true equilibrium.

Considering the mechanism of solidification of a liquid solution of magnesium and silicon (proportioned as  $\text{Mg}_2\text{Si}$ ) in aluminum it will be recalled that there first freezes out an aluminum-rich crystal resulting in an increasing concentration of magnesium and silicon in the liquid and ultimately, on final solidification, in the deposition of  $\text{Mg}_2\text{Si}$  or a eutectic of  $\text{Mg}_2\text{Si}$  and Al at the grain boundaries. When such an alloy is kept at a temperature slightly below that of the final solidification, some or all of the grain boundary deposit is taken into solution in the aluminum matrix, presumably, although not certainly, as separate atoms of magnesium and silicon. If, by lowering the temperature, the solid solution is made unstable, the solute atoms will aggregate into small particles of whatever second phase is most easily formed. As was pointed out in footnote 12, the probability of the formation of  $\text{Mg}_2\text{Al}_3$  seems greater than that of  $\text{Mg}_2\text{Si}$  in this instance.

The first phase to precipitate is not necessarily the most stable one that can form. Hence, it is to be expected, if  $\text{Mg}_2\text{Si}$  is more stable than  $\text{Mg}_3\text{Al}_2$ , the latter having been precipitated, that the Si atoms remaining in solution will, in time and under the proper conditions, react with the  $\text{Mg}_3\text{Al}_2$  to form  $\text{Mg}_2\text{Si}$  and reject the Al to the matrix. On the other hand, if the  $\text{Mg}_3\text{Al}_2$  is the more stable compound the insoluble excess of  $\text{Mg}_2\text{Si}$  in cast alloys should react with Al to form  $\text{Mg}_3\text{Al}_2$  at the grain boundaries. However, in view of the large amount of work that has been done on this system without the latter phenomenon having been observed, it appears most probable that  $\text{Mg}_2\text{Si}$  is the more stable of the two compounds.

If the above reasoning is correct, the phenomenon of the precipitation of  $\text{Mg}_3\text{Al}_2$  in an alloy of Al and  $\text{Mg}_2\text{Si}$  may be regarded as a case of metastable equilibrium. This is, of course, only a suggested explanation for which there is as yet no experimental support.

## An X-ray Study of the Nature of Solid Solutions\*

BY ROBERT T. PHELPS† AND WHEELER P. DAVEY,‡ STATE COLLEGE, PA.

(New York Meeting, February, 1932)

A STUDY of solid solutions has long been a source of interest because of the conditions controlling their formation. X-ray investigations so far have been conducted with the idea that there were two types of solid solutions. In the first type, an atom of the solute was supposed to replace an atom of the solvent in the crystal lattice. In the second type, an atom of the solute was supposed to lie in one of the interstices between the atoms of the solvent. These pictures both require that the sizes of the atoms must play an important part in the process of solution. It is the purpose of the present investigation to study the mechanism of solid solution, using pure silver as the solvent, and pure aluminum as the solute. X-ray measurements show that these elements have the same "shape" of atomic domains<sup>1</sup> (they both crystallize as face-centered cubes) and that their atomic diameters differ by less than one per cent.<sup>1</sup> The results of the present investigation point toward a chemical rather than a physical picture of the nature of solid solution, and make the older pictures merely special cases of a more general picture. The new theory has the advantage, too, that it offers a rational explanation of certain phenomena which hitherto have been only interesting detached facts.

The aluminum-silver system which was chosen for this study has been studied by various methods by several workers. By means of thermal analysis Gautier<sup>2</sup> and Petrenko<sup>3</sup> have determined the phase diagram. Hansen<sup>4</sup> studied the aluminum-rich alloys by means of thermal and microscopic analyses. He showed that at high temperatures silver dissolved in aluminum to the extent of 47 per cent by weight at 560° C. But this solubility decreased to 1 per cent at 200° C. Westgren and Bradley<sup>5</sup> made an extensive X-ray study of these alloys. They used the change in the lattice parameter of silver as a criterion of the solution

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<sup>1</sup> Davey: *Chem. Rev.* (1926) **2**, 349.

<sup>2</sup> Gautier: *Compt. rend.* (1896) **123**, 109.

<sup>3</sup> Petrenko: *Ztsch. anorg. Chem.* (1905) **46**, 49.

<sup>4</sup> Hansen: *Ztsch. f. Metallkunde* (1928) **20**, 217.

<sup>5</sup> Westgren and Bradley: *Phil. Mag.* (1928) **6**, 280.

of aluminum in silver. They found no change in the lattice parameter of aluminum which might be due to dissolved silver and concluded that the amount of silver dissolved must be very small. Hansen<sup>6</sup> showed that this is true at room temperature. Westgren and Bradley<sup>7</sup> also determined the crystal structure of the compound  $\text{Ag}_3\text{Al}$ . They found the other intermediate phase which Petrenko<sup>8</sup> thought to be a compound of the formula  $\text{Ag}_2\text{Al}$ , to be a solid solution of close-packed hexagonal structure which is homogeneous in the range of 86 to 92 per cent Ag. Mehl and Barrett<sup>9</sup> studied the Widmanstätten structures produced in high aluminum content alloys on suitable heat treatment.

In the present investigation we were only interested in the region of solid solution of aluminum in silver which is included in the range of 90 to 100 per cent Ag. We have studied the lattice parameter of a systematic series of solid solutions of aluminum in silver over this range and have compared the measured densities of these solid solutions with the theoretical densities as calculated from the current theories of solid solutions. These comparisons furnish new ideas for the picture of solid solution.

#### PREPARATION OF SAMPLES

The aluminum was of high purity (99.971 per cent) from the Aluminum Company of America. The impurities were: Si, 0.003 per cent; Fe, 0.012; Cu, 0.014.

The silver was prepared by the reduction of Baker's analyzed C.P. silver nitrate in a quartz tube through which hydrogen carefully purified to remove water vapor and oxygen was passed. The lattice parameter of this silver was the same as that of atomic weight purity silver as determined by Davey.<sup>10</sup> In order to prevent oxidation of the aluminum, the constituents were melted in a bath of Baker's analyzed potassium chloride in an alundum crucible. There was practically no reaction of either aluminum or silver with the potassium chloride, as was determined by melting each one separately in this flux. The loss of weight with either metal was less than 0.08 per cent. The loss in weight with any of the alloys did not exceed 4 mg. when the total weight was 6 grams. Chemical analyses by the Volhard method<sup>11</sup> on previously prepared aluminum-silver alloys agreed within 0.1 per cent with the composition calculated from the weight of the constituents. The method followed throughout in the preparation of these alloys was to keep the potassium

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<sup>6</sup> Hansen: *Op. cit.*

<sup>7</sup> Westgren and Bradley: *Op. cit.*

<sup>8</sup> Petrenko: *Op. cit.*

<sup>9</sup> Mehl and Barrett: *Trans. A. I. M. E., Inst. Met. Div.* (1931).

<sup>10</sup> Davey: *Phys. Rev.* (1925) **25**, 753.

<sup>11</sup> Popoff: *Quantitative Analysis*, Ed. 2, 135, Philadelphia, 1927. Blakiston's Son and Co.

chloride molten long enough to drive off such gases as might be present, add the aluminum and when this had melted, add the silver. Stirring was accomplished by removing the crucible with its contents from the furnace, shaking and rotating it so as to mix the molten metal and then putting it back in the furnace. This procedure was repeated twice and then the crucible was quickly cooled in air. The pellet was removed and remelted in potassium chloride and stirred twice by the method described above. After furnace cooling the alloys of 0.62 to 5.0 per cent Al content were forged to a 50 per cent reduction in thickness. The alloys of higher aluminum content could not be forged, because of their hardness and brittleness. The alloys were then heat-treated as noted in Table 1.

TABLE 1.—*Heat Treatment of Samples*

Sample No.	Aluminum Content, Per Cent	Heat Treatment
16a	0.62	Heated from room temp. to 700° C. in 11 hours. Heated at 700° C. for 24 hours. Cooled from 700° C. to room temp. in 12 hours.
17a	0.99	
18a	2.06	
19a	2.94	
20a	3.99	
21a	4.34	Heated from room temp. to 650° C. in 17 hours. Heated at 650° C. for 24 hours. Cooled from 650° C. to room temp. in 26 hours.
22a	5.04	
23a	6.04	
24a	7.05	
25a	7.69	
26a	7.99	
27a	9.07	

#### EXPERIMENTAL PROCEDURE

*Determination of Density of Alloys.*—Each small ingot was filed after the annealing process and then polished with fine emery paper to furnish a smooth surface. The surfaces of the ingots were scrubbed in absolute ethyl alcohol to remove any loose filings and grease. Just before weighing, the ingot was wiped with cotton wet with absolute ethyl alcohol and a platinum weighing basket and its suspension were rinsed in the absolute alcohol. The ingot was then placed in the basket and the whole assembly once more rinsed in the absolute alcohol. The densities were calculated by means of Archimedes' principle, using absolute ethyl alcohol whose density was determined, and corrected to *vacuo* at 25° C.

*X-ray Analyses.*—Filings were obtained from the alloy by means of a carefully cleaned file. The filings were placed in small quartz tubes which, in turn, were placed in a larger quartz tube which could be evacuated. The whole assembly was heated at 500° C. for 15 min. The filings that passed through a 200-mesh bolting cloth were mixed with

flour<sup>12</sup> in the ratio of 1 to 7 by volume and the resulting mixture was inserted into one half of a pyrex thin-walled capillary tube. The other half contained NaCl as a calibrating substance.<sup>13</sup> Diffraction patterns of these samples were obtained in the usual way by exposing them to the filtered radiation from the General Electric multiple diffraction apparatus<sup>14</sup> using the Coolidge type tube with the molybdenum target. The exposures varied from 24 to 72 hr., the time increasing with aluminum content. The tube current was 25 milliamperes. The lines on the resulting patterns were so well defined that the uncertainty of reading is  $\pm 0.1$  per cent. All measurements of distances are in terms of the lattice parameter of NaCl, 2.814 Å. The most probable lattice parameter for each film was obtained graphically by the method of Whipple.<sup>15</sup>

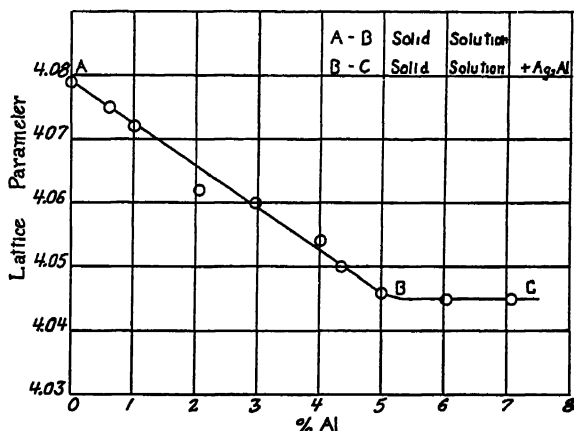


FIG. 1.—LATTICE PARAMETER OF ALLOYS.

#### DATA AND INTERPRETATION

*Lattice Parameters.*—The data for the lattice parameters of the solid solution phase are presented in Table 2. With the addition of increasing amounts of aluminum to silver the lattice parameter of the solid solution phase decreases in a regular manner as shown by Fig. 1. The diffraction pattern of a second phase appears faintly in the range between 5 and 6 per cent Al by weight. The curve in Fig. 1 indicates that this second phase begins to appear at 5.4 per cent Al. With further increase in aluminum content, the diffraction pattern of the solid solution became fainter, and the pattern of the second phase became stronger. When the aluminum content was 7.7 per cent by weight, the diffraction pattern of the solid solution phase disappeared and the pattern of the second phase

<sup>12</sup> Davey: *Gen. Elec. Rev.* (1925) **28**, 586.

<sup>13</sup> Davey: *Gen. Elec. Rev.* (1926) **29**, 121.

<sup>14</sup> Davey: *Gen. Elec. Rev.* (1926) **29**, 125.

<sup>15</sup> Whipple: *Jnl. Franklin Inst.* (1916) **182**, 37-205.

TABLE 2.—*Interplanar Spacings*

Plane	Sample No.									
	Pure Ag	16a	17a	18a	19a	20a	21a	22a	23a	24a
111	2.37	2.36	2.36	2.36	2.35	2.34	2.34	2.33	2.32	2.32
100	2.04	2.04	2.04	2.04	2.03	2.02	2.02	2.02	2.01	2.01
110	1.442	1.438	1.439	1.436	1.432	1.432	1.431	1.429	1.434	1.434
311	1.229	1.228	1.230	1.223	1.223	1.224	1.222	1.219	1.221	1.220
111(2)	1.177	1.177	1.177	1.170	1.170	1.171	1.169	1.167	1.169	1.169
100(2)	1.021	1.019	1.019	1.014	1.014	1.015	1.012	1.014	1.011	1.011
331	0.935	0.935	0.934	0.933	0.933	0.932	0.930	0.929	0.928	0.923
210	0.911	0.911	0.911	0.909	0.908	0.908	0.907	0.907	0.905	0.901
211	0.832	0.832	0.831	0.830	0.829	0.827	0.827	0.827	0.826	0.827
511; 111(3)	0.785	0.784	0.783	0.782	0.782	0.780	0.780	0.779	0.779	0.779
110(2)		0.721	0.720	0.718	0.717	0.717	0.717	0.716	0.716	0.714
531	0.689	0.688	0.688	0.687	0.686	0.686	0.685	0.684	0.683	0.684
100(3); 221	0.680	0.679	0.678	0.677	0.677	0.676	0.675	0.674	0.674	0.674
310	0.645	0.644	0.643	0.642	0.642	0.641	0.638	0.640	0.638	
533		0.622	0.620	0.619	0.618	0.618	0.617	0.617	0.616	
311(2)		0.614	0.613	0.612	0.611	0.611	0.610	0.617	0.608	0.607
Edge of unit cube. ....	4.079 Å ±0.004 Å	4.075 Å ±0.004 Å	4.072 Å ±0.004 Å	4.062 Å ±0.004 Å	4.060 Å ±0.004 Å	4.054 Å ±0.004 Å	4.050 Å ±0.004 Å	4.046 Å ±0.004 Å	4.045 Å ±0.004 Å	4.045 Å ±0.004 Å

was quite strong. A composition of 7.69 per cent Al corresponds to the intermetallic compound  $\text{Ag}_3\text{Al}$ . Between the limits of 5.4 and 7.7 per cent Al, no change was observed in the lattice parameter of the solid solution phase. In other words, the silver acted as though it were "saturated" with aluminum.

*Density.*—Curve *a* of Fig. 2 shows that the experimental densities of the solid solution of aluminum in silver (maximum error, 0.3 per cent) decrease linearly as the aluminum content is increased. This continues up to 6 per cent Al, for which the diffraction pattern shows a very small admixture of  $\text{Ag}_3\text{Al}$ . At an aluminum content of 7 per cent, the diffraction pattern shows a high proportion of  $\text{Ag}_3\text{Al}$ . At this point, curve *a* of Fig. 2 becomes displaced sharply to the right to give curve *c*. With further increase in aluminum, curve *c* continues downward, and is practically parallel with curve *a*. A comparison of curve *c* with an extrapolation of curve *a* shows that when the alloys are substantially 100 per cent  $\text{Ag}_3\text{Al}$  or  $\text{Ag}_3\text{Al} + \text{Al}$ , they have densities which are greater than they would have had if the alloys had been merely solid solutions of aluminum in silver.

In order to determine the mechanism of this solid solution we must compare our experimental densities with those calculated on the basis of various theoretical pictures. The theoretical pictures which have been considered will now be taken up in systematic order:

1. The possibility of a mechanical mixture of aluminum and silver crystals is ruled out because no diffraction lines which might be due to aluminum were observed on the X-ray films.

2. Using the picture that the aluminum atoms fit only in the interstices of the solvent atoms, all the calculated densities would have values greater than that of pure silver. This is partly because of the decrease in the lattice parameter and partly because of the additional mass introduced by the aluminum. It is evident, therefore, that this picture, too, must be ruled out.

3. Computation of the densities on the basis of a direct substitution of aluminum atoms for silver atoms in the solid solution lattice using the

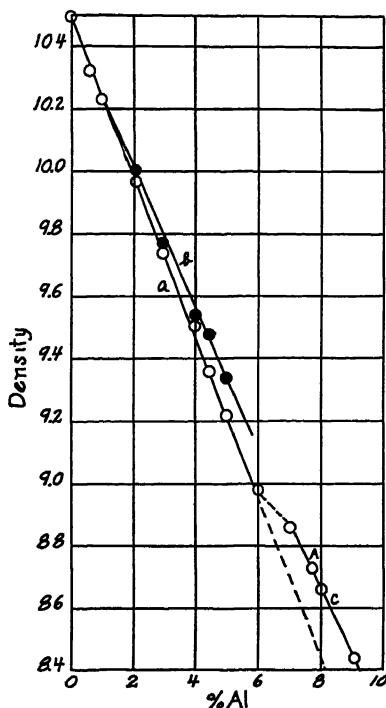


FIG. 2.—DENSITY OF ALLOYS.



observed lattice parameters gives values which fall along curve *b* of Fig. 2. These densities were calculated by means of the formula

$$\rho = \frac{n \times 1.65 \times 10^{-24}}{\left(\frac{a}{A} + \frac{b}{B}\right)d^3} \quad [1]$$

where  $\rho$  is the density of the alloy,  $n$  the number of atoms contained in an elementary cube (in this case 4);  $a$  and  $b$  are weight per cent of the two components,  $A$  and  $B$  their atomic weights and  $d$  the lattice parameter.

The maximum errors in the calculated densities are of the order of  $\pm 0.4$  per cent. The maximum errors in the experimental values are of the order of  $\pm 0.3$  per cent. Table 3 and Fig. 2 show that the experimental densities have values which are definitely somewhat lower than the corresponding calculated values. This discrepancy is more important than would appear at first sight. We would expect the actual density to be the combined result of two opposing tendencies. The decrease in the lattice parameter of the solid solution tends to increase the density. If we assume that the solid solution consists of a simple substitution of a relatively light aluminum atom for a silver atom in the crystal lattice, we would expect a tendency to decrease the density. Equation 1 shows that these two tendencies alone are not sufficient to account for the actual decrease in density. In order to reduce these theoretical densities to the actual experimental values, it is evident from the very definition of density that we must either (1) reduce the mass of our unit of structure, or (2) increase its volume, or (3) introduce an additional unit of structure of lower density which is not revealed in the diffraction patterns of the solid solutions. No other alternatives are possible.

TABLE 3.—*Comparison of Experimental Densities with Those Calculated by Equation 1*

Sample No.	Al, Per Cent	$a_0$	Experimental Density	Density Calculated by Equation 1
Pure Ag	0	4.079A	10.50	10.50
16a	0.62	4.075A	10.32	10.33
17a	0.99	4.072A	10.23	10.24
18a	2.06	4.062A	9.966	10.03
19a	2.94	4.060A	9.737	9.774
20a	3.99	4.054A	9.507	9.543
21a	4.34	4.050A	9.362	9.480
22a	5.04	4.046A	9.216	9.339
23a	6.04	4.045A	8.979	
24a	7.05	4.045A	8.858	
25a	7.69		8.733	
26a	7.99		8.662	
27a	9.07		8.441	

The first of these three alternatives is contrary to all chemical principles of constant atomic weights. The second must be discarded because the lattice parameters of the solid solutions are definitely fixed by the measurements of the diffraction patterns. This leaves us with the third alternative. There are two conceivable ways by which solid solutions might contain material not revealed by the X-ray diffraction pattern. It will appear that only one of these is tenable.

(a) Since the aluminum atom is slightly smaller than the silver atom, the atomic planes of silver might be assumed to be warped in the immediate neighborhood of the aluminum atoms. We cannot assume

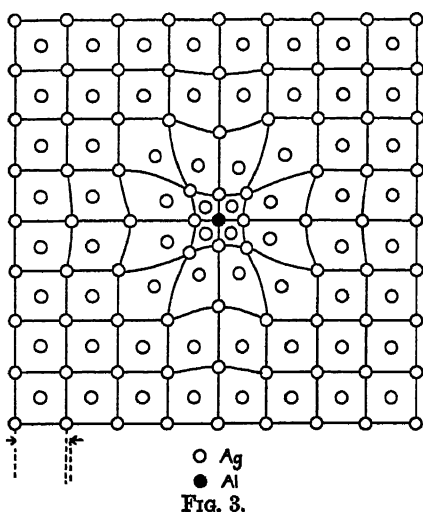


FIG. 3.

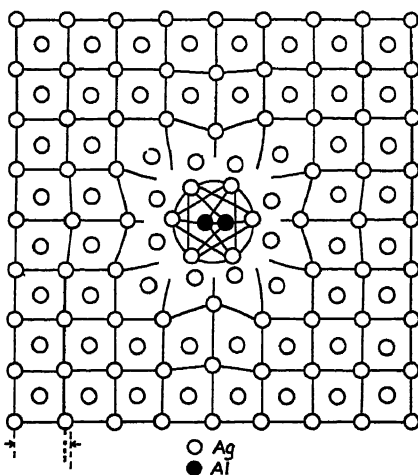


FIG. 4.

FIG. 3.—THE ORDINARY PICTURE OF SOLID SOLUTION (SHOWN TO BE UNTENABLE).

Lattice parameter of pure Ag is shown in lower left corner.

FIG. 4.—SCHEMATIC DIAGRAM SHOWING TRUE NATURE OF SOLID SOLUTIONS.

Lattice parameter of pure Ag is shown in lower left corner.

that there are no forces of attraction between the atoms of silver and aluminum, because there would then be very little tendency for the layers of silver to warp in to meet the aluminum. We would have the conditions represented by equation 1 which we have had to discard. If, however, we assume a loose kind of chemical attraction (perhaps of the secondary valence type<sup>18</sup>) between the atoms of silver and aluminum, we would have a distortion in the crystals such as shown in Fig. 3. The chains of silver atoms held together by the cohesive forces of the silver, would transmit the pull of the aluminum atoms to the rest of the crystal. The effect would be comparable to the pull of a rope tied around a bundle. Just as the bundle is put under compression, so the silver crystal would be put under compression. The regions near the aluminum atom would be distorted and so would not aid in producing any diffraction pattern.

<sup>18</sup> Westgren and Phragmen: *Trans. Faraday Soc.* (1929) 25, 379.

The portion of the silver crystal midway between adjacent aluminum atoms would show a smaller lattice parameter due to the compression. All this is consistent with the experimental fact that the diffraction pattern becomes weaker as the percentage of aluminum is increased, and with the fact that the lattice parameter becomes smaller. But this picture fails to meet our requirements, because it does not introduce into the silver the small amounts of *low density* material which we need in order to reduce the density calculated by equation 1 (curve *b* of Fig. 2) to the actual density (curve *a* of Fig. 2).

(b) We may assume that the solid solution represents actual chemical combination between every aluminum atom and the surrounding silver atoms. According to such a picture, we would expect the aluminum in solid solution in the silver to be  $\text{Al}^-$  and we would expect every  $\text{Al}^-$  to be accompanied by three  $\text{Ag}^+$  to give  $\text{Ag}_3\text{Al}$ .<sup>17</sup> We may assume that if the  $\text{Al}^-$  migrates in the crystal it can hand back a valence electron to one  $\text{Ag}^+$  and pick up one from a neutral atom in its path. In this way although we would always have the  $\text{Al}^-$  as part of  $\text{Ag}_3\text{Al}$ , it is not necessary to picture migrations for anything except the  $\text{Al}^-$ . If, during migration, two or more  $\text{Al}^-$  happen to fall into the correct spatial relationship for the crystal lattice of  $\text{Ag}_3\text{Al}$ , they will tend to stay there, thus forming tiny aggregates of  $\text{Ag}_3\text{Al}$ . In general these aggregates will be too small to give an X-ray diffraction pattern. (See Fig. 4.)

The size of these aggregates will be the resultant of two opposing tendencies: (1) a tendency towards disaggregation, which should be a function of the temperature, and (2) a tendency towards aggregation, which should be a function of the concentration of  $\text{Al}^-$ . Therefore, at any given temperature and concentration of  $\text{Al}^-$  a definite proportion of the  $\text{Al}^-$  will necessarily be in ionic dispersion in the silver, and the rest of the  $\text{Al}^-$  will be in the aggregates of  $\text{Ag}_3\text{Al}$ . The  $\text{Al}^-$  in ionic dispersion will contract the silver lattice as explained under (a). As the concentration of  $\text{Al}^-$  is increased, more and more of the silver will be in the form of  $\text{Ag}_3\text{Al}$  and will not contribute to the diffraction pattern of the compressed silver. More and more time should, therefore, be required to obtain diffraction patterns of the "solid solution." The direct measurement of the density of  $\text{Ag}_3\text{Al}$  (point A, Fig. 2) shows that such aggregates would serve our purpose as a low-density material which would reduce the density calculated by equation 1 (curve *b*, Fig. 2) to the actual density (curve *a*, Fig. 2).

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<sup>17</sup> At first sight it would seem from chemical theories of atomic structure that aluminum should have a negative valence of five. Considerations similar to those of J. J. Thomson (*Electron in Chemistry*, Franklin Inst. Philadelphia, 1923) make it seem that such an ion would be unstable and that  $\text{Al}^-$  is the most negative Al ion that can exist.

The predicted properties of our assumed structure of solid solution fit the experimental facts. Every other possible type of structure has been considered systematically, and has been ruled out. There seems, therefore, to be no escape from the conclusion that solid solution is chemical in its nature and that the atoms of the solute are in actual combination with the adjacent atoms of the solvent. If such a picture is adopted, it is possible to correlate several facts which have hitherto lacked a simple fundamental explanation.

It has long been known that the electrical conductivity of solid solutions is considerably less than that of the pure solvent metal. If the solute is in ionic combination with the solvent, an appreciable fraction of the valence electrons (which carry the electric current) are tied up to the negative ions of the solid solution. The valence electrons of the uncombined solvent can no longer travel directly along the potential gradient; they must travel around the aggregates of the ionic compound. The effect is as though the cross-section of the conductor were decreased and its length increased. Such a result would hardly have been predicted on the basis of the current pictures of solid solution.

Kremann and von Rehenburg<sup>18</sup> showed that molten solutions of sodium and potassium, zinc and antimony, bismuth and lead, and sodium and mercury can be electrolyzed against the back diffusion pressure in the liquid, so that analysis of the material frozen under the electrical field showed quite different proportions of the two metals at the two electrodes. The picture of metallic ions in molten solutions is entirely consistent with the picture of solid solutions which we have been forced to adopt. It would seem that Kremann and von Rehenburg would have had still more striking results if they had used solutions of metals like silver and aluminum, whose chemical properties would tend to give more strongly ionic intermetallic compounds.

In any case, if we accept the theory of solid solution which we seem to be forced to adopt, it would seem only reasonable to extend it to all solutions, including solutions of solids in liquids. A picture of this sort for liquid solutions is often hinted at in texts on physical chemistry and has received experimental support from the work of Jones and Getman,<sup>19</sup> Philip<sup>20</sup> and Scatchard.<sup>21</sup> If such an extension is to be made it would involve only negligible changes in the present equations for the lowering of the freezing point, etc., for dilute solutions, but should introduce important changes for concentrated solutions, because the ratio of solute to solvent would be altered by reason of the amount of solvent combined

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<sup>18</sup> Kremann and v. Rehenburg: *Ztsch. phys. Chem.* (1924) **110**, 559.

<sup>19</sup> Jones and Getman: *Amer. Chem. Jnl.* (1904) **32**, 327

<sup>20</sup> Philip: *Jnl. Chem. Soc.* (1907) **99**, 711.

<sup>21</sup> Scatchard: *Jnl. Amer. Chem. Soc.* (1921) **43**, 2406.

with the solute. It is well known that it is in the case of concentrated solutions that our present formulas fail.

It should be emphasized that the new picture of solid solution does not exclude the possibility of solid solutions of metals in which no compound can be detected by purely X-ray methods. We have already seen that the threshold concentration at which  $\text{Ag}_3\text{Al}$  gives a diffraction pattern is very high. Fig. 1 shows that the pattern does not appear at all until the aluminum content is 5.4 per cent by weight; 7.7 per cent Al by weight gives  $\text{Ag}_3\text{Al}$ . This means that the tendency toward aggregation is only slightly greater than the tendency toward disaggregation. It is only when the concentration of  $\text{Ag}_3\text{Al}$  has been built up to 70 per cent by weight of the alloy ( $\text{Ag}_3\text{Al}$  plus Ag) that the tendency toward aggregation becomes enough greater than the tendency toward disaggregation so that we find crystals sufficiently large to give X-ray diffraction patterns. It is reasonable to assume that solid solutions may exist in which the tendency toward aggregation of the intermetallic compound is still smaller than in  $\text{Ag}_3\text{Al}$ . It is conceivable that in some cases the tendency is so small that the diffraction pattern of the compound is never seen.

Several binary systems of metals are reported in the literature by various X-ray workers as being isomorphous over their entire range of composition. Among these may be mentioned as typical examples copper-gold,<sup>22, 23</sup> hydrogen-palladium,<sup>24</sup> silver-palladium<sup>25, 26</sup> and gold-palladium.<sup>27</sup> The first two have since been shown to give intermetallic compounds. The fact that there has been difficulty in demonstrating the existence of these compounds directly from X-ray diffraction patterns, or from thermal measurements, probably means that under ordinary conditions the tendency to aggregate is small. No positive statement can be made with regard to the systems silver-palladium and gold-palladium until comparisons have been made, similar to those presented here for silver-aluminum, between the calculated and the experimental densities.<sup>28</sup>

A picture of the mechanism of solid solutions in metals would not be complete without showing that it is consistent with the known facts of

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<sup>22</sup> Bain: *Chem. & Met. Eng.* (1923) 28, 21, 576.

<sup>23</sup> Ohshima and Sachs: *Ztsch. Physik* (1930) 63, 210.

<sup>24</sup> McKeehan: *Phys. Rev.* (1922) 20, 82.

<sup>25</sup> Astbury: *Nature* (1923) (London) 112, 53.

<sup>26</sup> McKeehan: *Phys. Rev.* (1922) 20, 424.

<sup>27</sup> Holgersson and Sedström: *Ann. Physik* (1924) 75, 143.

<sup>28</sup> Osawa [*Sci. Repts. Tohoku Imp. Univ.* (1926) 15, 619.] has reported on the relation between lattice constants and densities in nickel steels. His results cannot be used as criteria for or against the new picture of solid solutions, for he had 0.8 per cent carbon present. Nishiyama [*Sci. Repts. Tohoku Imp. Univ.* (1929) 18, 359.] measured the densities of certain binary alloys and the lattice constants of some of these. Unfortunately none of the alloys for which he gives both sets of data were of sufficient purity to make his data useful in connection with this picture.

solid solutions of salts containing a common ion, such as  $\text{AgCl-NaCl}$ , or  $\text{AgCl-AgBr}$ . Here it is well recognized that we are dealing with ions rather than with atoms. The obvious explanation of the progressive change in lattice parameter with percentage composition is that the electrostatic forces between the common ions and smaller of the two other ions tend to compress the crystal exactly as we have assumed that the ions of solute do in the metallic solid solution. From this point of view, the picture we have been forced to adopt as a result of studies of binary solid solutions differs from the one generally accepted for salts having a common ion only in the complications introduced by the presence of the common ion.

### SUMMARY

1. The solid solution of pure aluminum in pure silver lowers the lattice parameter of the silver by an amount which is proportional to the aluminum content of the solution. Saturation of aluminum in silver is reached at 5.4 per cent Al by weight. Further addition of aluminum gives aggregates of  $\text{Ag}_3\text{Al}$  of sufficient size to show X-ray diffraction patterns.

2. The experimental values for the densities of the solid solutions of aluminum in silver are somewhat lower than those calculated on the basis of a direct substitution of aluminum atoms for silver in the silver lattice. This discrepancy is greater than the combined error in the two values.

3. Systematic examination of the various possible types of explanation for this discrepancy leaves us with only one tenable theory—that the aluminum in the solid solution is chemically combined with the adjacent silver. If this explanation is used as the basis for a general theory of the nature of solutions, the picture is found to be consistent with the known facts. So far, it has not been found inconsistent with any known fact.

### ACKNOWLEDGMENTS

We are deeply indebted to the General Electric Co. for making available certain equipment without which this work would have been very difficult or even impossible. We are also indebted to the Aluminum Co. of America for the pure aluminum which we used, and for the analysis of the impurities it contained.

### DISCUSSION

*(Arthur Phillips presiding)*

J. S. MARSH, New York, N. Y. (written discussion).—By presenting precise data on a solid solution series, Messrs. Phelps and Davey make an important contribution. By presenting the theoretical significance of those data, they contribute substantially to the understanding of the far-reaching problem of solutions and their mechanism. Solutions and their mechanism, in a sense, embrace the one common denominator of the metallic state.

Before commenting upon the general significance of the paper, the writer wishes to suggest several more or less incidental revisions: (1) That the reasons for the heat treatment of Table 1 be given; (2) that the numerator of equation 1 be multiplied by 100; and (3) that the last paragraph on page 243 on required changes of critical point laws be expanded. It seems to imply that correction of concentration factors might remove much of the difficulty encountered when the several equations are applied to concentrated solutions. There is the further condition that the solution must be ideal. Application of the more rigorous equations (in which molecular species are recognized, of course) to many metallic systems shows them to behave as ideal solutions over considerable, or even all, ranges of concentration. The reason is seemingly that the factors which cause deviation in aqueous solutions are reduced to a minimum, or are absent, in many metallic solutions. It follows that metallic systems are the best possible proving ground for thermodynamic analysis. The point is emphasized in the hope that possible misinterpretation of the paragraph will be avoided.

The authors' diagrammatic explanation of the true nature of a solid solution is an especially pretty picture of what seems to be the *usual* mechanism of solid solution, but much remains to be done on the whole picture. Take, for example, the copper-palladium system, which is characteristic of a group. Thermodynamic analysis of the liquid-solid equilibria indicates that the solution is ideal from at least 30 atomic per cent to 100 per cent Pd, and that the solute is atomic Cu. (Other things are indicated also, but they have no bearing on the 30 to 100 per cent Pd range.) The crystal structure of rapidly cooled alloys is that of perfectly random distribution of atoms in a face-centered cubic lattice. Prolonged annealing below 400°C. of alloys in the vicinity of 50 per cent Pd results in the appearance of a body-centered phase which is homogeneous only within narrow limits. The astonishing part is that distribution is no longer random, for the copper atoms are at the center and the palladium atoms occupy the corners; *i. e.*, the CsCl type lattice appears. Is the phase a symmetrical solid solution of the true compound CuPd? For the present there is no answer satisfactory to everyone. The authors state that "it is conceivable that in some cases the tendency (to aggregate) is so small that the diffraction pattern of the compound is never seen." The writer prefers to add that there are cases in which atomic interaction is such that the solution is truly of the substitution type, although this is possibly only a limiting case of the authors' general picture.

The reason why certain structures are found so frequently at certain valence electron to atom ratios, pointed out by Hume-Rothery and Westgren and Phragmén, is yet to be explained satisfactorily, but the fact that they do remains. Causes and effects are difficult to distinguish. Probably the real key is to be found in energy relationships, but the physicist who investigates them is soon confronted with incomplete and often unreliable data, which makes verifications impossible. It is by achieving and maintaining high purity, then determining properties and constants by X-ray, thermal, electrical and other methods, that the store of data on alloys is being built up to the point that will enable the theoretical background to be completed. The necessity for that background is especially conspicuous in ferrous metallurgy. It is to be hoped that Dr. Davey's laboratory will continue to contribute.

C. S. BARRETT, Washington, D. C. (written discussion).—The authors do not state how their measurements compare with previous observations on these solid solutions, even though they refer to a paper by Westgren and Bradley in which the lattice parameters of two alloys containing the  $\alpha$  phase are reported. Westgren and Bradley found a 19 atomic per cent homogeneous  $\alpha$ -phase alloy to have  $a_0 = 4.056 \text{ \AA}$ , and the saturated  $\alpha$  phase coexistent with  $\beta'$  to have  $a_0 = 4.053 \text{ \AA}$ . The calculated density of the 19 atomic per cent alloy is 9.144, and if one assumes the parameter to be a linear function of atomic percentage of aluminum—an assumption quite in accord with the parameters reported in the present paper—the calculated density at the solubility

limit (21.7 atomic per cent, 6.48 weight per cent) is 8.948. These calculated densities are plotted on Fig. 5. The line through these gives the calculated densities throughout the solid solution range under the assumptions just mentioned. It is possible to draw this line in different ways corresponding to different assumptions regarding the variation of lattice parameter with composition, but I am not convinced that any of them show a significant discrepancy between calculated and observed densities.

There is some doubt as to the homogeneity of Westgren and Bradley's specimens, for they do not report giving their specimens an anneal to produce homogenization nor do they state whether the alloys were chill-cast or not. Yet the necessary precautions

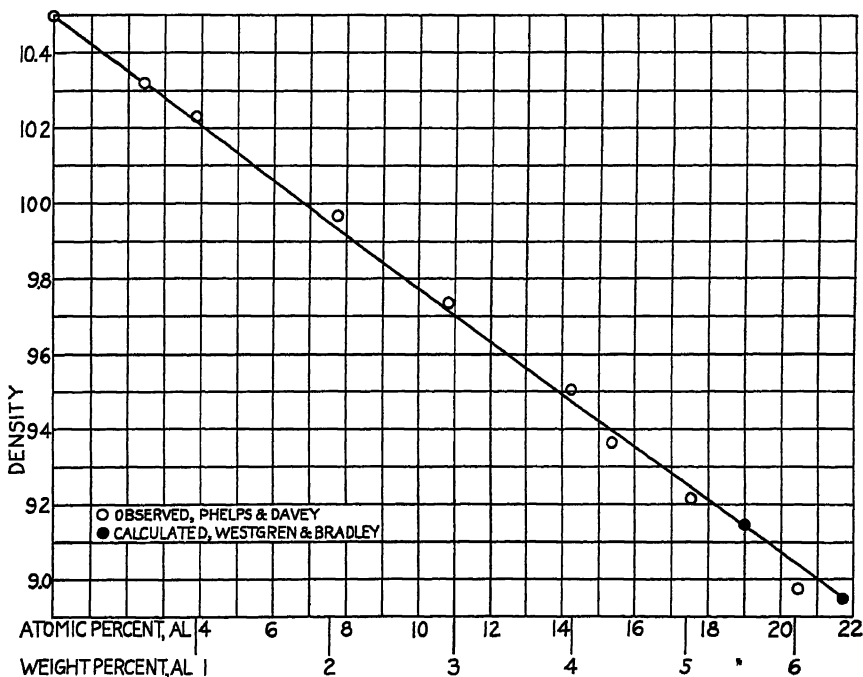


FIG. 5.

were undoubtedly known to the authors, for the work was published as recently as 1928. Their X-ray measurements were made with focusing cameras constructed by Phragmén and were capable of greater precision than the ones used here.

A. L. Norbury some years ago also proposed a type of solid solution in which the solute existed as molecules of an intermetallic compound having a different space lattice from that of the solvent.<sup>29</sup> On the basis of the amount of hardening produced by 1 atomic per cent of solute, he thought silicon in copper and sodium in lead should belong to this class. H. F. Kaiser and I found<sup>30</sup> that the observed densities of solutions of silicon in copper agreed with densities calculated from parameters determined on a precision camera, using in the calculations the simple substitutional theory of solid solution; there was no evidence for Norbury's molecular theory. The system lead-sodium has not been studied by X-rays from this standpoint, I believe.

<sup>29</sup> *Trans. Faraday Soc.* (1923-24) **19**, 586-600.

<sup>30</sup> *Phys. Rev.* (1931) **37**, 1697.



T. D. YENSEN, Pittsburgh, Pa. (written discussion).—For a number of years I have been trying to develop a physical picture of the crystal structure of alloys that may be helpful in our work. On a number of occasions<sup>31</sup> I have brought the subject up for consideration in the attempt to clarify the situation. Some of our theoretical friends have been very unsympathetic towards these efforts, as to them the mathematical formula is all that matters. Most metallurgists have been more or less indifferent. Only a few have manifested any marked interest. The present paper is, therefore, very welcome, as it forms a basis for further discussion.

I am in full agreement with the authors in regard to the conclusions of (b) on page 242, as will be seen by quotations from my recent papers:

1. "An intermetallic compound may consequently be regarded as a solid solution in which the forces of combination are stronger than those of diffusion. The stronger the former, the greater is the concentration range from which the compound is precipitated."<sup>32</sup>

2. Considering carbon in iron: . . . "we must assume, for concentrations less than 0.008 per cent, that carbon is *either* in solution or occurs as colloidal  $\text{Fe}_3\text{C}$  particles within the iron crystal, i. e., in a very diffuse state intimately connected with the iron lattice."<sup>33</sup>

3. In regard to oxygen in iron: . . . "Is it not clear, according to our definitions and present conceptions, if a compound ( $\text{FeO}$ ) is formed, that this compound is precipitated from the solid solution and can be identified under a sufficiently powerful microscope as a separate phase? . . . and a true solution would be possible only in case the impurity exists as atoms, . . . "<sup>34</sup>

I am delighted to have the authors restate these ideas in such clear, concise language as in their present paper. But even so, they have left room for misunderstanding, as I discovered in discussing the paper with a colleague some days ago. I would like, therefore, to emphasize still more the main points of the paper as I see them and ask the authors whether I give the correct interpretation:

1. An alloying element exists in a metal primarily as a chemical compound ( $\text{Ag}_3\text{Al}$  in this case). This is a separate phase or a precipitate, even though only colloidal in size.

2. Due to thermal agitation, however, dissociation takes place, and the resulting atoms (or ions) migrate (or diffuse) through the metal lattice to become attached to some other atoms as they pass along. These migrating atoms (or ions) constitute the portion of the alloying element that is in true solid solution and consequently vary with the temperature.

3. The stronger the bond between the atoms and the lower the temperature, the longer proportion of the time the compounds will exist; consequently the lower will be the solubility. As a typical example may be mentioned  $\text{Fe}_3\text{C}$  in iron.

Conversely, if the strength of the bonds between the atoms of the two elements is of the same order of magnitude as that of the atoms of each of the elements, there will be no appreciable tendency towards the formation of distinct compounds, and if they are formed, the coupling will be too loose to prevent dissociation and diffusion. The result in such cases is that the atoms of the alloying element will be in a state

<sup>31</sup> a. *Trans. A. I. M. E., Iron and Steel Div.* (1929) 320.

b. *Phys. Rev.* (1932).

c. *Amer. Soc. Steel Treat.* (1931).

d. *Amer. Soc. Steel Treat.* (1932).

<sup>32</sup> Reference of footnote 31, a, 326.

<sup>33</sup> Reference of footnote 31, b.

<sup>34</sup> Reference of footnote 31, c.

of diffusion most of the time (or "disaggregation" as the authors state it) and there will be a high degree of true solid solubility. Nickel in iron is a typical example.

It should be observed, however, that as the temperature drops the rate of diffusion also drops, and may actually stop altogether at room temperature, so that the crystal structure observed at room temperature will be, even in such alloys, a result of the rate of cooling. Rapid cooling from elevated temperatures may give one structure while slow cooling may give a different one, depending upon the potential energy-temperature relations.

R. S. DEAN and J. KOSTER, Washington, D. C. (written discussion).—The authors have reported some valuable experimental results and have drawn interesting conclusions in regard to the relations existing between solid solutions and compounds in metallic systems. However, we feel that their data will permit a somewhat different interpretation and that their assumption of the formation of disperse particles of compound in the alloys of low aluminum content is not quite justified.

In 1900, Nernst wrote that the differences between physical mixtures and chemical compounds are differences in degree only, and that between them, all gradations occur.<sup>35</sup> Some few years later Rinne pointed out that isomorphous mixtures behave as transition members between chemical compounds and physical mixtures.<sup>36</sup> This similarity has long been qualitatively recognized and still forms a matter of controversy among those men interested in the nature of the solid state.

The introduction of the X-ray method of crystal analysis has permitted the clarification of some of our ideas concerning the formation of "mixed crystals," "solid solutions" or isomorphous mixtures, as the phenomenon has been variously called. Data from X-ray determinations together with density measurements have led to the conception that two types of solid solutions are possible. The first is formed by the simple substitution of atoms or ions of the solute into the lattice of the solvent. In the second, the solute particles are believed to be much smaller and hence able to fit into the interstices between solvent particles. These two ideas are well enough recognized to require no extended discussion at this time.

Closely akin to the substitution theory of solid solution are the theories of isomorphism and its relation to the size and polarization properties of the constituent particles of two isomorphous crystals. Goldschmidt<sup>37</sup> has shown rather definitely that isomorphism arises when the relative sizes of the crystal "Bausteine" and their relative polarization effects are, within certain limits, equal. The significance of this statement may be seen from considerations of compounds of the general formula,  $Ab_2$ . If we concern ourselves with ions which are not greatly polarized (i.e., distorted) in one another's presence, it can be shown that the ratio of the ionic radii of  $A$  and  $B$  has considerable influence on the type of structure assumed by the crystal. If the ratio  $R_A:R_B$  is greater than 0.67, crystals of the calcium fluoride type are found. If this ratio lies between 0.4–45 and 0.67, the structure usually belongs to the rutile type. However, if a polarizable ion, that is, one easily polarized, is put into a structure with a partner capable of inducing considerable distortion, the above ratios no longer hold.

Such "laws" as the one above imply at first sight that atomic radii are constant regardless of the particular compound being studied. This is not necessarily true for compounds of different ionic characteristics. It is generally true, however, that typically ionic compounds such as the alkali halides do show that various ions may

<sup>35</sup> Nernst: Theoretische Chemie, Ed. 3, 32. 1900.

<sup>36</sup> Rinne: Centr. Mineral. Geol. (1919) 161.

<sup>37</sup> Goldschmidt: Die Geochemischen Verteilungsgesetze der Elemente, pt. VII. Oslo, 1926.

be bound together in different combinations and apparently maintain radii which vary but slightly in the different cases.

Another empirical deduction along this line is of importance in relation to the formation of solid solutions. When the radii of "Bausteine" do not differ by more than 15 per cent, isomorphous miscibility over a wider range of concentrations results.<sup>38</sup> The apparent radii used in making such deductions have generally been obtained at room temperatures, hence we might expect the rule to refer to similar temperatures. Potassium chloride and sodium chloride are "isomorphic"; they both have the same lattice type and have many similar properties. The radius of the  $K^+$  ion is shown to be 1.33 Å while that of  $Na^+$  is 0.98 Å, and of  $Cl^-$  is 1.81 Å. The system  $NaCl$ - $KCl$  forms a continuous series of solid solutions when formed from the melt, the curve showing a minimum at 664° for the equimolecular mixture. This decomposes into two phases<sup>39</sup> at 405°, and at room temperatures exists as a mechanical mixture of  $KCl$  and  $NaCl$ . This is in accord with the above statement relative to the differences between the ionic radii, which in this case amounts to  $1.33 - 0.98 = 0.35$  or about 36 per cent of the smaller. The  $Cl^-$  ion is presumably the same in both salts. However, potassium chloride and potassium bromide form a continuous series of solid solutions even at room temperature. Here the  $K^+$  ion is fixed, and the difference between the radius of  $Br^-$  ion and the  $Cl^-$  ion is  $1.96 - 1.81 = 0.15$ , or 8.3 per cent of the smaller, which is in agreement with the rule for isomorphous miscibility. It thus seems possible to substitute for all of the  $Cl^-$  ions in  $KCl$  an equal number of  $Br^-$  ions and to cause no pronounced change other than a slight stretching of the lattice parameter. The  $K^+$  lattice remains fixed. In  $KCl$ , each  $K^+$  ion is surrounded by 6  $Cl^-$  ions at equal distances. Anywhere between 100 per cent  $KCl$  and 100 per cent  $KBr$  each potassium ion will be surrounded by six ions which may or may not be alike. If we regard a definite lattice type as one criterion of solid compounds, we may look upon such a system as  $KCl$ - $KBr$  as a sort of chemical compound of variable composition. From an atomistic standpoint, it is essentially a three-component system; the intermediate stages might be called ternary solid solutions.

It has been pointed out by Wyckoff<sup>40</sup> that the supposition that two crystals form solid solutions with one another only when their molecular volumes are similar has long been in existence. The same author goes on to show that the "similarity in molecular volume" (or interatomic distances) is not the factor that determines the degree of solid miscibility of structurally isomorphous crystals. This is shown, for instance, by the following example: "metallic copper and metallic gold have face-centered cubic arrangements of atoms with a nearest approach of 2.55 and 2.88 Å respectively, and mix in all proportions in the solid state; but sodium and potassium chlorides, with identical atomic arrangements and with distances between nearest atoms of 2.81 Å and 3.13 Å are immiscible at room temperature. The molecular volume of the miscible gold is 44 per cent greater than that of the copper; that of the immiscible potassium chloride, on the other hand, is only 37.6 per cent more than sodium chloride." Such reasoning is the direct result of the conception that mixed crystals of two binary compounds are mixtures of two distinct molecular species, and of two distinct lattices. Actually, however, we must look at systems of this sort not as mixtures of two molecules, but as mixtures of three atoms (or ions). This is very important on the basis of the picture of a solid solution which we wish to present.

<sup>38</sup> Reference of footnote 36.

<sup>39</sup> Bruni and Meneghini: *Atti ist Veneto* (1911) 71, II, 195.

<sup>40</sup> Wyckoff: *The Structure of Crystals*, 405. New York, 1924. Chemical Catalog Co.

A simple solid solution is more or less a dispersion of the solute particles as individuals throughout a lattice whose general architecture is determined solely by the solvent.

TABLE 4.—*Percentage Difference between Radii for Pairs of Metals Known to Form Unbroken Series of Solid Solutions*

System		Radii, Ångströms		Difference, Ångströms	Difference (percentage of smaller)
A	B	A	B		
Cu	Au	1.28	1.44	0.16	12.5
Cu	Mn	1.28	1.38	0.10	7.8
Cu	Ni	1.28	1.24	0.04	3.2
Cu	Pt	1.28	1.38	0.10	7.8
Cu	Pd	1.28	1.37	0.09	7.0
Ag	Au	1.44	1.44	0	0
Ag	Pd	1.44	1.37	0.07	5.1
Au	Pd	1.44	1.37	0.07	5.1
Mg	Cd	1.55	1.52	0.03	2.
Pb	In	1.74	1.57	0.17	11.
Sb	Bi	1.61	1.82	0.21	13.1
Mn	Fe	1.38	1.27	0.11	9.
Mn	Co	1.38	1.26	0.12	9.5
Mn	Ni	1.38	1.24	0.14	11.3
Fe	Co	1.27	1.26	0.01	0.8
Fe	Ni	1.27	1.24	0.03	2.4
Fe	Pt	1.27	1.38	0.11	8.7
Co	Ni	1.26	1.24	0.02	1.6
Co	Cr	1.26	1.28	0.02	1.6
Ni	Pd	1.24	1.37	0.13	9.7
Li	Cd	1.57	1.52	0.05	3.3
Le	V	1.27	1.36	0.09	7.9

If we apply the law of isomorphous miscibility and its relation to the sizes of the participating atoms as expressed by Goldschmidt to the binary metal systems, we find that the agreement is very good. Table 4 shows the percentage difference between radii for various pairs of metals which are known to form unbroken series of solid solutions. In no case is the difference greater than the prescribed 15 per cent. Table 5 shows similar figures for systems which are reported by Tammann as forming no solid solutions. It can be seen that the converse of Goldschmidt's rule does not hold in all cases. In calculating the figures in these tables, the radii as determined by Goldschmidt have been used and are those referring to the element in the uncharged state and for coordination No. 12. It is generally agreed that the units of any metallic lattice are ions. And the tables of radii usually show that an atom which has lost one or more electrons is considerably smaller than the uncharged atom. However, the atomic radii computed from the lattices of the pure metals are much larger than those deduced for the same metals in most inorganic compounds. This would seem to indicate that metal lattices are not built of ions in the same sense that NaCl is built of ions and that the state of individual particles in metals is more nearly that of uncharged atoms. But we cannot be too literal in our acceptance of atomic radii in spite of their pronounced usefulness.

Solid solutions may be formed in two ways: by crystallization from the liquid and by diffusion in the solid condition. Diffusion in metallic (solid) systems generally

TABLE 5.—*Percentage Difference between Radii for Systems Reported by Tammann as Forming No Solid Solutions*

System		Radii, Ångströms		Difference, Ångströms	Difference, Percentage
A	B	A	B		
Cu	Mg	1.28	1.60	0.32	25.
Cu	Tl	1.28	1.71	0.43	33.6
Cu	Pb	1.28	1.74	0.46	36.
Cu	Bi	1.28	1.82	0.54	42.1
Cu	Cr	1.28	1.28	0	0
Ag	Pb	1.44	1.74	0.30	20.8
Ag	Fe	1.44	1.27	0.17	13.4
Ag	Co	1.44	1.26	0.18	14.3
Ag	Cr	1.44	1.28	0.16	12.5
Au	Pb	1.44	1.74	0.30	20.8
Au	Sb	1.44	1.62	0.17	11.8
Mg	Zn	1.60	1.37	0.23	16.8
Mg	Sn	1.60	1.58	0.02	1.2
Mg	Pb	1.60	1.74	0.14	8.8
Mg	Sb	1.60	1.61	0.01	0.6
Mg	Bi	1.60	1.82	0.22	13.8
Mg	Ni	1.60	1.24	0.36	15.
Zn	Tl	1.37	1.71	0.34	24.8
Zn	Pb	1.37	1.74	0.37	27.
Zn	Sb	1.37	1.61	0.24	17.5
Cd	Al	1.52	1.43	0.09	6.3
Cd	Tl	1.52	1.71	0.19	12.5
Cd	Sb	1.52	1.61	0.09	5.9
Cd	Bi	1.52	1.82	0.30	19.7
Al	Ti	1.43	1.71	0.28	19.5
Al	Sn	1.43	1.58	0.15	10.5
Al	Pb	1.43	1.74	0.31	20.7
Al	Bi	1.43	1.82	0.39	27.2
Tl	Pt	1.71	1.38	0.33	24.
Sn	Bi	1.58	1.82	0.24	15.2
Pb	Mn	1.74	1.38	0.36	26.
Pb	Fe	1.74	1.27	0.47	37.
Pb	Co	1.74	1.26	0.48	38.2
Pb	Cr	1.74	1.28	0.46	36.
Bi	Mn	1.82	1.38	0.44	31.8
Bi	Fe	1.82	1.27	0.55	43.6
Bi	Co	1.82	1.26	0.56	44.5
Bi	Cr	1.82	1.28	0.54	42.

follows the ordinary laws of isotropic diffusion and several measurements of the diffusion coefficient have been made. Some of the data are shown in Tables 6 and 7. The diffusion tendency is a function of the temperature and it would be expected that

it would become zero at the absolute zero. The recent work of Hevesey and Seith<sup>41</sup> indicates that diffusion does indeed become very small at low temperatures; but extrapolation of their results to  $-273^{\circ}\text{C.}$ , which is scarcely justified in view of the small temperature range over which they worked, permits a finite diffusion at that temperature. The point that is important to the theory of solid solutions is that

TABLE 6.—Data from Hevesey and Seith<sup>a</sup>

Au in Pb		Ag in Pb		Bi in Pb	
Temp.	<i>D</i>	Temp.	<i>D</i>	Temp.	<i>D</i>
182	$3.6 \times 10^{-3}$	182	$3.2 \times 10^{-4}$	182	
203	$6.6 \times 10^{-3}$	203	$7.5 \times 10^{-4}$	203	$5.6 \times 10^{-5}$
227	$1.0 \times 10^{-2}$	227	$1.5 \times 10^{-3}$	227	$4.9 \times 10^{-5}$
253	$1.8 \times 10^{-2}$	253	$3.2 \times 10^{-3}$	253	$4.4 \times 10^{-5}$
282	$2.7 \times 10^{-2}$	282	$7.1 \times 10^{-3}$	282	$4.1 \times 10^{-5}$
315	$4.9 \times 10^{-2}$	315	$2.0 \times 10^{-2}$	315	$3.6 \times 10^{-4}$

Tl in Pb		Sn in Pb		Pb in Pb	
Temp.	<i>D</i>	Temp.	<i>D</i>	Temp.	<i>D</i>
144		144		144	$4.2 \times 10^{-10}$
162		162		162	$3.2 \times 10^{-9}$
182				182	$1.3 \times 10^{-8}$
203	$3.2 \times 10^{-6}$	203	$4.2 \times 10^{-7}$	203	$7.1 \times 10^{-8}$
227	$8.3 \times 10^{-6}$	227	$1.3 \times 10^{-6}$	227	$3.3 \times 10^{-7}$
253	$2.0 \times 10^{-5}$	253	$4.9 \times 10^{-6}$	253	$1.7 \times 10^{-6}$
282	$5.6 \times 10^{-5}$	282	$1.8 \times 10^{-5}$	282	$8.2 \times 10^{-5}$
315	$1.3 \times 10^{-4}$	315	$7.5 \times 10^{-5}$	315	$4.2 \times 10^{-5}$

TABLE 7.—Data from Other Authors

Au in Pb <sup>a</sup>		Au in Ag <sup>b</sup>		C in Fe <sup>c</sup>	
Temp.	<i>D</i>	Temp.	<i>D</i>	Temp.	<i>D</i>
100	0.000042				
165	0.004				
200	0.7				
		870	0.000037	925	0.010

<sup>a</sup> Roberts-Austen: *Proc. Roy. Soc.* (1896) 59, 283.

<sup>b</sup> Fraenkel and Henten: *Ztsch. f. anorg. u. allgem. Chem.* (1921) 116, 1.

<sup>c</sup> J. Runge: *Ztsch. f. anorg. u. allgem. Chem.* (1921) 116, 1.

<sup>41</sup> H. Hevesey and W. Seith: *Ztsch. f. Elektrochem. u. angew. phys. Chem.* (1931) 37, 528.

diffusion takes place at all. The data in Table 6 for the diffusion of thallium in lead can be fitted to an equation which is:

$$\log D = 0.0145T - 8.530$$

All of the figures given in Table 6 have been read from the curves published by Hevesey and Seith as no numerical data were given in the original article. The diffusion of thallium in lead has been chosen in the present instance because it seems to be in approximately the middle of the list in so far as the value of  $D$  is concerned. At room temperature we find from the above equation that the diffusion constant  $D$  for thallium in lead should be about  $5.2 \times 10^{-4}$  sq. cm. per day. This means that 5.2 grams  $\times 10^{-4}$  of thallium will pass across 1 cu. cm. of alloy per day when the difference in concentration is 1 g. per cubic centimeter per centimeter length. This is equivalent to:

$$\frac{5.2 \times 10^{-4} \times 6.06 \times 10^{23}}{204.39} \text{ atoms of thallium per day.}$$

This proves to be  $1.5 \times 10^{18}$  atoms per day or  $6.4 \times 10^{18}$  per hour. Unquestionably they do not move in straight lines, hence the amount of migration is probably rather great, even at room temperatures. When the concentration gradient becomes zero, diffusion ceases. This means, obviously, nothing more than that the "foreign" atoms have reached some sort of kinetic equilibrium throughout the mass of the solvent. All further motion of the thallium particles, be they atoms or ions, has ceased as far as our usual means of observation are able to tell us. But we cannot postulate that this saturated solid solution, which is the result of such a process, is in a static condition. Individually the thallium particles are still moving from place to place. It is reasonable to believe that at any instant, the distribution of foreign atoms is quite uniform. And it would be illogical to believe that they will only migrate along certain crystallographic planes. The lead lattice is of the face-centered cubic type; its coordination number is 12; there are no preferred planes in so far as atomic surroundings are concerned; and lastly the thallium atom differs from the lead atom but slightly in size. In such a kinetic system and under a state of true equilibrium, we cannot have anything other than a statistical distribution of the thallium atoms. Since the two atoms are of such similar sizes, and since it is generally agreed that atoms are not mutually interpenetrable, and remembering that the face-centered lattice is rather closely packed, we are forced into postulating motion of some sort for the solvent atoms. This state of affairs represents to our mind that obtaining in a true solid solution. It is essentially kinetic. The actual migratory motions do not necessarily involve velocities of the same order as obtain in gases or liquids. The solute atoms are uniformly distributed in a sort of superstructure as first proposed by Tammann, but with the difference that the superstructure is not fixed in relation to any one point in space and hence cannot produce any separate diffraction effects. A thallium atom is in say the (111) plane now. After some period of time the same atom might be found in a position contributing to the (100) plane. The usual X-ray picture requires at least 30 min. During this time the thallium atom may have moved but from the corner position in one of the cubes to the center of one of the faces nearest to it, and no pattern would be produced which could be assigned to that particular atom. And likewise for all the solute atoms. Perhaps the only contribution which these wandering atoms supply to the diffraction phenomena is an increase or decrease in the average intensity of reflections from all of the planes. We are frequently led to forget, owing to the diagrams offered by the crystallographers, that the only static property of crystals is the system of imaginary lines and points constituting the lattice proper. We have not yet found a method of tagging individual atoms so as to prove whether or not the members of a lattice of a pure crystal migrate and shift positions. And if diffusion is known to occur, we must assert that both solvent and solute are in a state of motion.

Perhaps we might be able to determine something about the distribution of solute particles in solid solutions by means of X-ray pictures at liquid-air temperatures. We know of no record of such tests but they would prove most interesting in the present connection.

Such a picture of a slow-moving superstructure will permit an explanation of Tammann's reaction limits.<sup>42</sup> This investigator found that various oxidizing and etch reagents affected gold-copper alloys up to sharply defined limits in terms of the gold content. They were usually found to be multiples of  $\frac{1}{8}$  mol of gold per mol of alloy. This observation led Tammann to propose the "superstructure" for the gold atoms. But he seemed hesitant about accepting a kinetic picture since it was found that ordinary amounts of time did not cause further attack after a limit had been reached. A slow shifting, as we have put forth here, would answer as an explanation.

It has been mentioned<sup>43</sup> that alloys of copper and gold of compositions 75 per cent Cu, 25 per cent Au (atomic per cent) give X-ray powder photographs which indicate a regularity of distribution between the two kinds of atoms. The same effect is obtained for alloys of 75 per cent Au and 25 per cent Cu. These atomic percentages correspond to  $\frac{3}{8}$  mols solute per mol of solvent, hence the result is very pertinent to the interpretation of the reaction limits mentioned above.

If the process of fusion of an alloy which forms a solid solution is arrested at some temperature above complete solidification, we know from the equilibrium diagram that a solid phase of one composition is in equilibrium with the liquid of a somewhat different composition. In the following, we shall consider only simple solid solutions of one element in another. Suppose that we take as an example the silver end of the silver-aluminum system. Here we have a solid solution up to some 4 or 5 per cent Al, the liquidus and solidus meeting at a point corresponding to the compound  $Ag_3Al$ . This section of the diagram is shown in Fig. 6. The spread between the compositions of the liquid and the solid at any one equilibrium temperature is due to the difference in internal energy between the two phases. If we assume that the melt has, to begin with, a composition as indicated by A in Fig. 6, we know that at some temperature slightly below the melting point of pure silver, such as  $t_1$ , a small number of crystallites will form. At the instant of formation of the crystallites the melt had the composition A. And the equilibrium diagram is without meaning unless the aluminum atoms are statistically distributed throughout the liquid just before the occurrence of the infinitesimal temperature drop producing the separation of the solid. Unless we postulate some very hurried shifting of the atoms in the neighborhood of the center of crystallization of each crystallite, we must believe that the solid which separates has, at the instant of its formation, the same distribution of aluminum ions as the liquid. The actual volume of solidifying material is very small. Crystallites may be imagined to form in regions near aluminum atoms as well as between aluminum

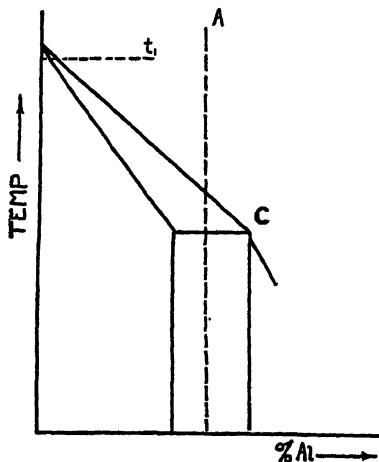


FIG. 6

<sup>42</sup> Tammann: Textbook of Metallography. Trans. by Dean and Swenson, 305. 1925.

<sup>43</sup> E. C. Bain: *Chem. & Met. Eng.* (1923) 28, 21.



atoms. The number of silver atoms predominates in the melt. Those crystallites forming "between" the aluminum atoms will predominate over those which form near to (and hence carry with them) some of the aluminum particles. As a result, immediately after this process, more aluminum atoms per atom of silver will be found in the melt. And likewise the solid will have a smaller ratio of aluminum to silver than in the original melt.

The mobility of either kind of atom in the liquid is more than likely rather high, consequently the liquid probably readjusts its distribution to another statistical state corresponding with its new composition. If we confine ourselves to consideration of the equilibrium diagram this readjustment must occur. If the temperature is dropped in infinitesimal steps, the above process is repeated until the point *C* is reached. Just before the final solidification of the remainder of the melt at this point, the liquid has the composition corresponding to that of the compound  $\text{Ag}_3\text{Al}$ . Statistically, the "structure" of the liquid is necessarily very similar, in so far as the coordination numbers of the two atoms are concerned, to that of the solid compound. At no time during our hypothetical thermodynamically reversible cooling is it possible for the liquid, or the solid, for that matter, to have the same "structure" as prevails at the point *C*. That is, such an alloy, cooled under equilibrium conditions, will have but a very slight probability of forming the compound until the point *C* is reached. And if it were cooled quickly, we would expect to obtain a supersaturated or undercooled solid solution with even less chance of compound formation.

Zwicky<sup>44</sup> has recently pointed out that the persistence of direction in crystals is perhaps the real force back of crystal formation and the one which accounts for the sharp transition of liquid-crystal. By statistical mechanical reasoning he arrives at the conclusion that "paradoxically—those forces which determine the primary structure of a crystal are not at the same time responsible for the crystal formation itself." The primary structure signifies the coordinate arrangement as the six  $\text{Cl}^-$  ions around each  $\text{Na}^+$  ion in  $\text{NaCl}$ , and vice versa. According to this view, such arrangements are involved in the melts before solidification occurs. There are hence two energy factors involved in the crystallization process. One corresponds to the formation of the "primary structure" and the other to the process of alignment of these primary structures. It has been shown that certain glasses "are available which prove that liquids may, in fact, be in a lower energy state than the corresponding crystal,"—that is to say the energy of alignment has not been called into play in the formation of the glass.

This conception of primary structure is similar to the one we have offered above in the case of aluminum-silver alloy. We might go on to point out the morphology of the situation at the instant of compound formation. If  $\text{Ag}^+$  ions are placed at the corner of a face-centered cube and  $\text{Al}^-$  ions in the faces, the ratio of  $\text{Ag}$  to  $\text{Al}$  is 3 to 1, just as it is in the compound  $\text{Ag}_3\text{Al}$ . A unit cell containing two molecules of  $\text{Ag}_3\text{Al}$  can be formed from two  $\text{Al}^-$  ions at diagonally opposite corners and the six silver ions in the faces. If the sizes of the ions are different, this structure readily swings over into a hexagonal crystal, which may be seen by turning the "cube" so as to look at it from one corner, perpendicular to the octahedral plane.

It might prove interesting to determine whether the compound  $\text{Ag}_3\text{Al}$  would form by diffusion in the solid state and at total concentrations less than 7.69 per cent  $\text{Al}$  as required by the ratio 3  $\text{Ag}$  to one  $\text{Al}$ . If not, we could safely conclude that the compound does not form unless the average distribution corresponds to the primary structure we have discussed above. Tammann<sup>45</sup> has heated and compressed a mixture of

<sup>44</sup> Zwicky: *Proc. Nat. Acad. Sci.* (1931) 524.

<sup>45</sup> Tammann: *Ztsch. f. anorg. Chem.* (1906) 51, 330.

powdered bismuth and thallium. After heating for 5 hr. at  $165^{\circ}$ , a yellow border of  $\text{Bi}_2\text{Te}_3$  is seen to form between the bismuth and a saturated solid solution at the grain boundaries. This is an interfacial phenomenon, and to determine anything about the distribution of solute atoms in a solvent by means of any diffusion process it will perhaps be necessary to start with a single crystal of the solvent.

To recapitulate: a picture of a solid solution is offered in which the solute atoms migrate slowly from place to place. While the migration is slow at room temperatures, it is, nevertheless, sufficiently rapid to prevent detection of the solute ions by means of the usual X-ray procedure. In general, the distribution of solute will be rather uniform and probably might be visualized as a slow motion picture of monatomic gas molecules in a mixture with another monatomic gas. The influence of such a statistical arrangement on the formation of intermetallic compounds is discussed.

It might be pointed out that the chief difference between a solid solution and a chemical compound is that migrating ions may shift from one crystallographic position to another in the solution, whereas in the compound, which is generally distinguishable by a different lattice, the grouping is such that shifts can take place only between like atoms. This stability of the lattice of the compound is a consequence of the size and relative distortions of the constituent atoms which seem also to be the determining factors in the type of structure assumed.

The mechanism by which the solute atom decreases the parameter of the solvent lattice is pictured by the authors as the effect of a sort of rope tied around a bundle. From the discussion above, we would have to make this a moving rope. For systems of high symmetry the electrostatic forces decrease as a high power of the distance. The local distortions are thus probably rather great but all that the X-ray method determines is nothing more than the time average of the interionic distances. These high local distortions around each ion of aluminum necessarily produce a region of low density between two neighboring aluminum ions, and it cannot be expected that equation 1 of the authors will apply exactly. The differences between the calculated and experimental densities are readily explainable on the basis of these mobile regions of low density coupled with the grosser crystal defects found in all actual crystals. It is not necessary to postulate an additional low-density material. The statement of the authors to the effect that two or more  $\text{Al}^{+}$  might "happen to fall into the correct spatial relationship for the crystal lattice of  $\text{Ag}_3\text{Al}$ " seems, to our mind, to represent a state of very high improbability.

The authors' discussion of electrical conductivity is somewhat confusing. They are apparently speaking of the greatly lowered conductivity due to solid solution and yet they say that the electrons must travel around "aggregates of ionic compounds." When such aggregates are present it seems illogical to consider the alloy a homogeneous solid solution. As a matter of fact the trend of recent work is to indicate that solid solutions when free from such aggregates do not have markedly lower conductivity than the pure solvent but that when they break down to give "aggregates of ionic compounds" the conductivity drops sharply. The important thing here is that when we have aggregates we have interfaces. The explanation of the electrical and mechanical properties and density of supersaturated solid solutions (and it is difficult to study any other kind at room temperature) is to be sought in these interfaces or secondary structures. Mr. Gregg and one of the present writers<sup>46</sup> presented a theory of hardening based on the properties of these interfaces before this society several years ago. We suggested then that the properties of alloys or metals having large interfacial areas could be explained by the formation of a type of pseudocompound in which electrons were shared between metallic atoms. This was made possible by the forced separation

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<sup>46</sup> Dean and Gregg: *Proc. Inst. Metals Div., A. I. M. E.* (1927) 368.

of metallic atoms to a greater or shorter distance than the normal lattice distance. Such separations might very well correspond to the regions of low density we have mentioned above and a certain fraction of the electrons are thus prevented from taking part in the general exodus of the remaining free electrons under the influence of the applied potential.

F. N. RHINES, New Haven, Conn. (written discussion).—The statement is made (p. 242, line 34) that "the direct measurement of the density of  $\text{Ag}_3\text{Al}$  (point A, Fig. 2) shows that such aggregates would serve our purpose as a low-density material which would reduce the density calculated by equation 1 (curve b, Fig. 2) to the actual density (curve a, Fig. 2)." If a plot is made of aluminum content vs. calculated density assuming any desired percentage of association of  $\text{Al}^-$  and  $\text{Ag}^+$  as  $\text{Ag}_3\text{Al}$  of density indicated at point A of Fig. 2, and the remaining  $\text{Al}^-$  substituted in the silver lattice giving it a density determined by equation 1, it will be found that all values of density fall on curve b of Fig. 2 or on its projection. For example:

Assume an alloy with 5 per cent Al and take a case in which 75 per cent of the Al is combined as  $\text{Ag}_3\text{Al}$ . Then 3.75 per cent Al is associated with 49.45 per cent Ag as  $\text{Ag}_3\text{Al}$  of molecular weight 350.61. There will remain 1.25 per cent Al in solid solution with the other 45.55 per cent Ag. The density of the 53.2 per cent of combined material will be 8.733 determined experimentally as the density of  $\text{Ag}_3\text{Al}$ . The density of the 46.8 per cent of solid solution can be determined by the use of equation 1:

$$O = \frac{4 \times 1.65 \times 10^{-24}}{\left( \frac{97.33}{107.88} + \frac{2.67}{26.97} \right) (4.4046 \times 10^{-6})^3} = 9.956$$

Whence  $53.2 \times 8.733 + 46.8 \times 9.956 = 9.305$  is the calculated density of the alloy. By comparison with Fig. 2 it will be seen that this value falls very close to curve b. Any other assumption of composition and degree of association will result in a density value falling on curve b.

This follows naturally from the coincidence that point A lies on the extension of curve b of Fig. 2. Therefore the aggregate of  $\text{Ag}_3\text{Al}$  cannot serve as the low-density material necessary to reduce the density calculated by equation 1 to the actual density. Moreover if the  $\text{Al}^-$  in solid solution is assumed to be situated as in Fig. 3 the calculated density must obviously be even farther from the measured density.

A. STANSFIELD, Montreal, Que. (written discussion).—I have read this paper with great interest and in view of the importance of the subject I am taking the liberty of contributing to the discussion, although I am not in close touch with X-ray investigation.

The authors find that the density of alloys of silver with from 2 to 5 per cent of aluminum is distinctly less than would be predicted on the assumption that the aluminum atoms replace atoms of silver in the crystal lattice. They conclude that the aluminum combines with silver to form small aggregates of the compound  $\text{Ag}_3\text{Al}$  and they explain the abnormally low density of these alloys by the presence of this compound which has a smaller density. In giving this explanation the authors apparently forget that if some of the aluminum atoms are segregated in  $\text{Ag}_3\text{Al}$  aggregates, the remainder of the alloy will contain less than the average proportion of aluminum and will therefore have a higher density. The low density of the compound will be offset by the high density of the rest of the alloy and cannot be used in explanation of the abnormally low density of the whole alloy.

Fig. 2 shows that the density of alloys of 7 or 8 per cent of aluminum, which consist largely of  $\text{Ag}_3\text{Al}$ , lies very nearly on the line of the predicted density of the solid solution alloys and, in relation to the aluminum content, the  $\text{Ag}_3\text{Al}$  alloys are actually

denser than the solid solution alloys. It is clear, therefore, that the low density of the latter cannot be explained by the density of  $\text{Ag}_3\text{Al}$ .

The presence in a silver alloy of small aggregates of a different crystalline form may, however, explain the lightness of these alloys in another way. Around each of these aggregates there must be a space which is incompletely filled by silver atoms, as indeed is suggested in Fig. 4, and this incomplete filling will lessen the density of the alloy. With larger percentages of aluminum, when the compound is assembled in larger aggregates, there will be fewer vacant spaces and the density will again become normal.

Formula 1, which is used to calculate the density of solid solution alloys, is not given quite correctly. The factor  $10^{-24}$  in the numerator is the cube of  $10^{-8}$ , the size of the Ångström unit, which occurs in the denominator. This would be correct provided  $a$  and  $b$  are taken as the weight *per unit* of the component metals, but if they are taken as *percentages*, as is stated in the paper, the calculated density is 100 times too small and it would be necessary to use the factor  $10^{-22}$  in the numerator.

H. E. STAUSS, Newark, N. J. (written discussion).—The authors are led to formulate changes in the theory of solid solution because of the discrepancies that they observe between the measured and calculated densities of their alloys. It should be pointed out that their data can be explained in accord with the usual theory of solid solution. Up to and including 4 per cent Al, their alloys show discrepancies in density that are less than the experimental errors. It is only for the alloys containing 4.34 and 5.04 per cent Al that the differences can be maintained to be real. Now the phase diagram published in the International Critical Tables (2, 400) based on the work of Petrenko shows the compound forming at 4 per cent Al. The density measurements of the authors are in full accord with the diagram and may be considered to confirm it. Their results do not agree with the diagram only in that they failed to find evidence of the compound by means of X-ray diffraction patterns.

The obvious explanation for the failure to detect the second phase is that X-ray analysis is less sensitive than the methods of metallurgical analysis proper. The only way of determining the relative sensitivities of the two methods is by using them on the same alloy system. In the case of silver-aluminum series, it can be maintained that the test shows the methods of metallurgical analysis to be the more sensitive. In order to explain their results, the authors themselves assume X-ray diffraction to be less sensitive than the comparison of densities.

It is usually assumed that X-ray analysis is at least as sensitive as the other methods of analysis. Westgren, for example, comes to this conclusion.<sup>47</sup> However, the laws governing alloys are so little known that it is unwise to rely upon generalizations and each alloy still deserves individual attention. In these particular alloys, the X-ray diffraction patterns failed to reveal a second phase in the region in which other analysis had indicated it. It is not proposed to defend Petrenko's diagrams as necessarily correct; but it has already been pointed out that the authors' density measurements are in agreement with it, and, therefore, the diagram does merit careful consideration. The actual boundary between the solid solution field and the two-phase field, however, is not decided by the presence of diffraction lines due to the compound, but by extrapolation of the lattice parameter-composition curves (Fig. 1). The authors have done this by assuming two straight-line relations that intersect at 5.4 per cent Al. If, in spite of the large absolute experimental errors, it is assumed that the relative errors are small, the curves can be drawn as shown in Fig. 7. Now the intersection occurs at about 4 per cent Al, in agreement with the other experimental results. The curve may seem peculiar, but it has the advantages of passing through all experimental points and of not forcing the data to fit an assumed curve.

<sup>47</sup> *Trans. A. I. M. E., Inst. Metals Div.* (1931) 13.

Thus, it is possible to interpret the authors' data in accord with the usual theory of solid solution. This is being emphasized because all data concerning, and all methods of attack upon, the problem of the structure of metals should be considered from every possible angle.

YAP, CHU-PHAY, New York, N. Y.—I am not concerned with building up a mechanistic picture; I am interested in treating the problem in terms of energy changes; *i.e.*, thermodynamics.

In a recent paper<sup>48</sup> I have shown that the heat of solution of  $\text{Fe}_3\text{C}$  in the melt is

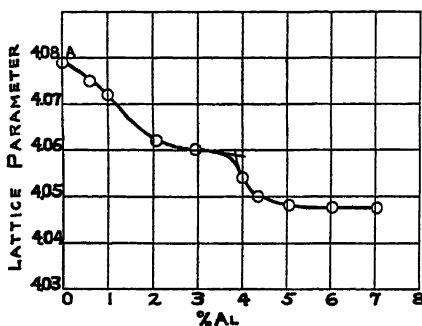


FIG. 7

practically identical with its heat of solution in austenite and inasmuch as the solute in the melt is unquestionably  $\text{Fe}_3\text{C}$ , the conclusion that the solute in austenite is  $\text{Fe}_3\text{C}$  is inescapable. My view is that the  $\text{Fe}_3\text{C}$  is molecularly dispersed and it has, therefore, no crystalline structure of its own. A simple consideration of the energy involved in the process of dissolution of  $\text{Fe}_3\text{C}$  either in the melt or in austenite supports this view. Suppose we have a melt in equilibrium with solid  $\text{Fe}_3\text{C}$  (*i.e.*, saturated with  $\text{Fe}_3\text{C}$ ); then the change in the molal free energy of formation of  $\text{Fe}_3\text{C}$  ( $\Delta F$ ) is equal to its partial molal free energy ( $\Delta \bar{F}$ ) in solution in the melt. Keeping in mind the fact that intermetallic compounds are nonpolar, the total energy change involved in dissolving a mol of  $\text{Fe}_3\text{C}$  in the melt and then dissociating it to its components, Fe and C, is equal to its heat of formation minus the heat necessary to bring about a change of state from solid to liquid (fusion). The latter is always very much smaller than the former and as the compound is formed with an absorption of heat (endothermic), the heat of solution should, therefore, be reasonably expected to be a fairly large exothermic quantity—that is, the compound gives off heat upon going into solution. This is not, however, the case. Hence, the reasonable conclusion is that  $\text{Fe}_3\text{C}$  is dissolved in the melt (as well as in austenite) as such in molecular dispersion.

As there is perhaps still some question regarding the free energy of formation of  $\text{Fe}_3\text{C}$ , let us take another example and view the problem from an entirely different angle. I have already shown elsewhere that the change in the free energy of formation of  $\text{FeO}$  at  $1000^\circ\text{C}$ . is about  $-43,000$  cal. per mol; hence the dissociation pressure of the compound at that temperature is about  $10^{-15}$  atm. In other words, the compound does not dissociate at all, and yet we cling, almost violently in some quarters, to the view that the solute in iron saturated with  $\text{FeO}$  is oxygen and not  $\text{FeO}$ . Since the solution is saturated and is in equilibrium with solid  $\text{FeO}$ , the partial molal free energy ( $\Delta \bar{F}$ ) must also be  $-43,000$  cal. per mol. If  $\text{FeO}$  is dissociated to oxygen and iron upon solid solution, it is easy enough to construct a perpetual engine of the first class, by simply dissolving a little more  $\text{FeO}$  in solid solution by raising the temperature, then lowering it again and repeating the operation.

It is rather difficult to understand how such simple thermodynamic considerations as the above have never been taken into account in constructing a picture of the nature of solid solutions. It seems dangerous to lay so much emphasis on purely mechanistic pictures, as has been done by X-ray crystallographers.

<sup>48</sup> Yap, Chu-Phay: A Thermodynamic Study of the Iron-carbon System in the Solid and Liquid States, II. *Trans. Faraday Soc.* (1931) 27, 790.

A word more in regard to aggregation and dispersion. It can be easily shown on thermodynamic grounds that a dispersed state does not necessarily mean an unstable state. Theoretically, in a system in which all the dispersed particles are of the same size (that is, of the same surface energy) there should be no tendency towards aggregation; it is only due to the difference in the surface energy of the particles of varying sizes that we have a tendency towards aggregation, which may follow either of two paths leading to equally stable systems, viz., (1) a system in which the dispersed particles finally aggregate into a single particle and (2) a system in which all the particles assume the same size.

W. P. DAVEY (written discussion).—We are glad that Mr. Marsh has given us the chance to correct the explanation of the symbols  $a$  and  $b$  of equation 1. "Weight per cent" often is used erroneously in the literature to mean "weight fraction," and we have unfortunately fallen into the same error. The latter phrase should be substituted in the text.

The samples of solid solution were forged and heat-treated to insure as perfect homogeneity as possible. If this had not been done, our alloys might justly have been suspected of containing microscopic segregations of  $\text{Ag}_3\text{Al}$ . The absence of such segregations was essential to our interpretation of the data. The cooling mentioned in Table 1 was very slow in order that our alloys might represent equilibrium at room temperature. If this had not been done, our alloys might have been suspected of having been undercooled from some state which was stable at some higher temperature.

The changes required in the laws of liquid solutions are already well known to physical chemists and in the case of electrolytes are included along with other corrections in their so-called activity coefficients. In a few cases of liquid solutions of nonelectrolytes (see references 19, 20, 21) they have corrected only for the compound formation between solvent and solute. This is done by merely subtracting from the original amount of the solvent the amount which is combined with the solute, and then using this smaller quantity of solvent in the standard equations for solutions. Mr. Marsh's statement that metallic solid solutions show themselves to be "ideal" solutions if our picture is taken into account is a strong argument in favor of our picture.

We are taking steps to study the copper-palladium system as suggested by Mr. Marsh.

We doubt whether Westgren and Bradley's specimens, mentioned by Mr. Barrett, were pure enough or homogeneous enough to give sufficiently accurate X-ray data on the nature of solid solutions. Unless we go to a "back reflection" method (or possibly to a properly calibrated Seeman-Bohlin camera) it is hard to get higher reproducibility of X-ray results than are obtained by the use of the  $\text{NaCl}$  comparison standard, which gives a limit of reproducibility of 0.1 per cent.

We are glad to have the added confirmation to our picture from the type of experiments (different from ours) which Mr. Yensen has been conducting. We believe that Mr. Yensen has restated our case very well except that we do not like to think of undissociated ions wandering around in what Mr. Yensen calls "true" solid solution. We prefer to think of these ions as always attached to some atom (ion) or atoms (ions) of the solute—in their wanderings they merely unattach themselves from an atom (ion) of solute on one side and immediately attach themselves to another atom (ion) on the other side. The effect is, according to our picture, like climbing a rope "hand-over-hand"—letting go at one point only to catch hold at another. In other words, except for the infinitesimal time interval between letting go of an atom on one side and combining with another atom on the other side, we feel that we should always consider the wandering atom (ion) of solute to be in chemical combination with solvent. Such a picture enables us to take advantage of the low density of each

*molecule* of the compound in accounting for the discrepancy between the actual density of the solid solutions and the density as calculated from the older pictures.

From the discussion by Mr. Rhines, it is evident that we have not made our argument sufficiently clear. A restatement in somewhat different language may help:

1. In order to account for the low density we must imagine a source of low-density material in the alloy.

2. Only three sources of such a low-density material can be imagined: (a) Al atoms, (b) "molecules" of  $\text{Ag}_3\text{Al}$ , (c) crystals of  $\text{Ag}_3\text{Al}$ . The following shows that only one of these is tenable.

Equation 1 is derived on the basis of aluminum atoms replacing silver atoms in accordance with the older theories. It is evident from Fig. 2 that the presence of aluminum atoms alone can not account for the low density. Nor can we expect the aluminum to introduce new voids into the crystal which will lower the density, for the aluminum atom is smaller than the silver atom. Possibility (a) must therefore be discarded.

It is hardly to be expected that "molecules" of  $\text{Ag}_3\text{Al}$  would fit into an Ag lattice without leaving extra voids around the edges. This is brought out in Fig. 4. If the density of  $\text{Ag}_3\text{Al}$  is not too big to counterbalance the effect of these voids, then possibility (b) must be retained. The experimental facts of Fig. 2 show that  $\text{Ag}_3\text{Al}$  has a density lower than that of solid solution of aluminum in silver, so that there is nothing unreasonable for the case of possibility (b) in assuming for the  *$\text{Ag}_3\text{Al}$  molecules plus their surrounding voids* a density which would fall on curve *a* of Fig. 2.

In the special case where the density of the intermetallic compound falls on an extension of curve *b* of Fig. 2, the crystals of the compound would give densities for the solid solution falling along curve *b*. The only condition calling for a still lower density than that given by curve *b* would be the presence of the so-called "amorphous layer" (transition layer) between the compound and the solvent metal. If the crystals are of any appreciable size, the effect of the "amorphous layer" is negligibly small in comparison with the effect of the crystals. It is to be expected, therefore, that, since the silver-aluminum system seems to fall under this special case, curve *c* of Fig. 2 will be practically an extension of curve *b*, as indeed it is, within experimental error. Possibility (c) must therefore be discarded solely because the silver-aluminum system happens to fall under the special case outlined above.

The extra-low density of curve *a* should, therefore, only appear in that range of temperature and composition for which disaggregation exceeds aggregation; i.e., in the range where our picture calls for a "molecular" dispersion of  $\text{Ag}_3\text{Al}$  in the solvent Ag. This range is covered by curve *a* of Fig. 2. Instead of being an objection to our picture, the points brought out by Mr. Rhines really constitute a portion of the reasoning which leads to our picture. We are grateful to Mr. Rhines for providing us with an opportunity to further clarify the statements in our paper.

We believe that the points raised by Dr. Stansfield have already been taken care of in the replies to other discussions, especially that of Mr. Rhines. The next to the last paragraph in Dr. Stansfield's remarks, instead of being a competing picture, deals with just the very picture we are trying to propose.

Concerning the points raised by Mr. Staus, we are not much worried that we found our first  $\text{Ag}_3\text{Al}$  at 5.4 per cent Al instead of at the 4 per cent indicated by the Petrenko diagram. The greater the precautions used to insure homogeneity, the higher will be the percentage of aluminum required to show the  $\text{Ag}_3\text{Al}$  phase. The upper limit of 7.7 per cent, of course, is set by the proportions required to make  $\text{Ag}_3\text{Al}$ . The whole purpose of our Fig. 1 is to find the true limit of the so-called solid solubility. This curve shows that under our conditions the  $\text{Ag}_3\text{Al}$  phase existed between the limits of 5.4 and 7.7 per cent Al.

Our argument as to the nature of solid solution rests upon a comparison of experimental and calculated densities, and not on the proportion of aluminum required, under the conditions of our experiments, to make  $\text{Ag}_3\text{Al}$  appear as a so-called separate phase. Table 3 shows that our calculated densities correspond to the lattice parameters which were found by direct experiment—not to points read off from some curve such as Fig. 1. We find considerable difficulty, therefore, in agreeing with Mr. Stauss' last paragraph.

Mr. Yap finds that  $\text{Fe}_3\text{C}$  occurs in the *melt*. We agree with him that it would be quite extraordinary if  $\text{Fe}_3\text{C}$  occurred in molecular form in the melt and then magically changed to  $3\text{Fe} + \text{C}$  in the solid. Mr. Yap's results, then, afford excellent confirmation to our picture of solid solutions.

We are well acquainted with the data presented by Mr. Dean and Mr. Koster, and with the hitherto accepted theory of solid solutions which they have so ably summarized in their discussion. Unfortunately, the theory to which they adhere does not conform to the data which they present, for it would require silver and aluminum to be mutually soluble in all proportions since the two atomic radii differ by less than one per cent. It was this discrepancy between the actual facts and the old theory which caused us to perform the experiments described in our paper. The new theory which we have proposed is not only consistent with the old experimental data, but it is also consistent with the new data. It is essentially a kinetic type of theory.

The rest of Dean and Koster's discussion seems to be a plea for reserving the term "solid solution" for the state required by the old theory and for inventing a new name for the state postulated by the new theory. Matters of nomenclature must always be matters of opinion; they can not be settled by debate. It will therefore be sufficient for us to say that since the state required by the old theory is naturally included as one extreme (probably unattainable) of the state required by the new theory, it seems to us better to retain the old name to describe a long list of well known alloys rather than to confuse the literature with a new term.



# On the Theory of Formation of Segregate Structures in Alloys\*

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(New York Meeting, February, 1932)

IN a series of papers published recently,<sup>1</sup> R. F. Mehl and associates have studied the characteristics of form and orientation of many segregate structures and have found diversified conditions which can be explained only by postulating some specific kind of cooperative mechanism permitting the matrix lattice in some favorable region to transform into the segregate lattice in an adaptable region presenting a geometrically similar arrangement of atoms. We have collected the published data on crystallographic relationships of this sort, chiefly derived from Mehl's work, in Table 1.

It is evident at once that the crystal structure of the matrix does not uniquely determine the location of the plate structures or other forms assumed by the segregate. Thus, the first seven items in the table represent precipitation of platelike forms from a matrix of face-centered cubic structure, but these plates are found stratified along planes of form  $\{111\}$ ,  $\{100\}$ ,  $\{110\}$  or another unidentified form, depending upon specific conditions involving the nature and concentration of the segregating substance. Again, in a matrix of body-centered cubic structure, plates, needles or stars have been found and the favored inner surface of segregation may be a plane of form  $\{110\}$ ,  $\{112\}$ ,  $\{210\}$ , or indeed a surface without crystallographic indices defining a bundle of close-packed lattice lines (strings of atoms) taken more or less at random. Such a surface might be formed ideally by revolving one of these parallel strings of atoms around another as an axis.

Hanemann and Schröder<sup>2</sup> recently discussed these questions, principally with relation to original conceptions concerning the process of

\* From a part of a dissertation to be presented by D. W. Smith to the Faculty of the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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<sup>1</sup> R. F. Mehl and C. S. Barrett: Studies upon the Widmanstätten Structure, I. *Trans. A.I.M.E., Inst. Metals Div.* (1931) 78.

R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structure, II. *Idem*, 123.

R. F. Mehl, C. S. Barrett and F. N. Rhines: Studies upon the Widmanstätten Structure, III. See page 203.

<sup>2</sup> Hanemann and Schröder: On the Origin and Structural Development of Segregates in Metallic Solid Solutions. *Zisch. f. Metallkunde* (1931) 23, 269, 297.

TABLE 1.—*Crystallographic Relationship of Segregate to Matrix*

Matrix	Segregate		Principal Surface of Separation Between Matrix and Segregate				Location of Selected Lattice Lines of Densest Atom Packing		Source of Data
	Identity	Form	(1) In Matrix	(2) In Segregate	Orientation of (2) on (1)	(1) In Matrix	(2) In Segregate		
Face-centered cubic taenite of meteoric iron, Fe-Ni	Body-centered cubic Kamacite	Plates	Planes of form {111}	Planes of form {110}	Probably {111} of {110}    {110} of {111}	[110] in plane of separation, 3 directions	[111] in plane of separation, 2 directions	Young <sup>a</sup>	
Face-centered cubic solution of Fe-C (austenite)	Tetragonal martensite or body-centered cubic ferrite	Plates	Planes of form {111}	Planes of form {110}	{111} of {110}    {110} of {111}	[110] in plane of separation, 3 directions	[111] in plane of separation, 2 directions	Kurdjumov and Sachs <sup>b</sup>	
Face-centered cubic solution of Al-Ag	Hexagonal close-packed $\gamma$ solution	Plates	Planes of form {111}	Planes of form {0001}	{10 $\bar{1}$ 0} or {0001}    {110} of {111}	[110] in plane of separation, 3 directions	{10 $\bar{1}$ 0} in plane of separation, 3 directions	Mehl and Barrett <sup>c</sup>	
Face-centered cubic solution of Cu-Si	$\gamma$ solution	Plates	Planes of some 12 family form					Mehl and Barrett <sup>c</sup>	
Face-centered cubic solution of Al-Cu	Tetragonal CuAl <sub>3</sub>	Plates partly spheruloidized	Planes of form {100} and of some other (undetermined form)	Some evidence of planes of form {001}	Possibly {120} of {001}    {011} of {100}	[110] in plane of separation, 2 directions		Mehl, Barrett and Rhines <sup>d</sup>	
Face-centered cubic solution of Al-Mg-Si	Uncertain Al <sub>3</sub> Mg <sub>2</sub> , Mg <sub>2</sub> Si or Si	Plates	Planes of form {100} and also {110}			[110] in plane of separation, 2 directions in {100} and 1 in {110}		Mehl, Barrett and Rhines <sup>d</sup>	
Face-centered cubic solution of Fe-C (austenite)	Body-centered cubic ferrite	Plates	Planes of form {111}			[110] in plane of separation, 3 directions		Belavew <sup>e</sup>	

TABLE 1.—(Continued)

Matrix	Segregate		Principal Surface of Separation Between Matrix and Segregate				Location of Selected Lattice Lines of Densest Atom Packing		Sources of Data
	Identity	Form	(1) In Matrix	(2) In Segregate	Orientation of (1) on (2)	(1) In Matrix	(3) In Segregate		
Body-centered cubic solution of N in Fe	Fe <sub>3</sub> N?	Plates	Planes of form {210}			Smallest angle between a [111] and plane of separation 15°		Mehl and Barrett <sup>c</sup>	
Body-centered cubic solution of Zn in Cu	Face-centered cubic $\alpha$ brass	Needles	Surface of revolution around [111] or {566}?			[111] in surface of separation. 1 direction		Mehl and Marzke <sup>e</sup>	
Body-centered cubic solution of Zn in Cu	Face-centered cubic $\alpha$ brass	Plates	Planes of form {112}?			[111] in plane of separation. 1 direction		Phillips <sup>d</sup>	
Body-centered cubic solution of Zn in Cu	Cubic $\gamma$ brass	Stars and polyhedra	Planes of form {110}			[111] in plane of separation. 2 directions		Mehl and Marzke <sup>e</sup>	
Body-centered cubic solution of Al in Cu	Face-centered cubic $\alpha$ solution	Needles	Surface of revolution around [111] or closely similar direction			[111] in surface of separation. 1 direction		Mehl and Marzke <sup>e</sup>	

<sup>a</sup> Young: *Proc. Roy. Soc.* (1926) 112, 630.<sup>b</sup> Kurdjumov and Sachs: *Zisch. Physik.* (1930) 64, 325.<sup>c</sup> Mehl and Barrett: *Trans. Am. Inst. M. E., Inst. Met. Div.* (1931) 78.<sup>d</sup> Mehl, Barrett and Rhines: *A. I. M. E. Preprint* (1932).<sup>e</sup> Belaw: *Jnl. Inst. Metals* (1923) 29, 379.<sup>f</sup> Mehl and Barrett: *Metals and Alloys* (1930) 1, 422; also reference of footnote c.<sup>g</sup> Mehl and Marzke: *Trans. Am. Inst. M. E., Inst. Met. Div.* (1931) 123.<sup>h</sup> Phillips: *Discussion. Trans. A. I. M. E., Inst. Met. Div.* (1931) 152.

diffusion, and took the position that the specific crystal structure of the segregate should have no important influence on the shape of the segregate, although a process of rearrangement (recrystallization) may follow the initial formation of the segregate and bring about some changes.

Hanemann and Schröder introduce the term, "perfusion," to represent a directed diffusion in which atoms of one kind move in rows through voids in the lattice. This form of movement is considered generally possible when the crystal structure shows the two kinds of atoms, each arranged in continuous rows, as in the case of beta brass of copper-zinc atomic ratio 1:1, or when the structure shows atoms of a dissolved element occupying some of the available positions on lattice lines in the interstices between the atoms of the solvent, as with carbon in gamma iron. The beta copper-zinc lattice, possessing a structure in which zinc atoms and also copper atoms are in rows perpendicular to the sides of the cube, thus has three "perfusion" directions in which either zinc or copper atoms may be considered capable of movement into or out of a segregate in process of formation. In a case of this sort it is considered that adjacent rows (zinc and copper) may exchange atoms as required to bring about the necessary concentration adjustment between solvent and segregate.

It is now demonstrated that the direction of growth of a segregate needle formed under the influence of "perfusion" in several directions must be along an axis of symmetry for these three directions. The conditions may be visualized by reference to the simple stereographic projection of Fig. 1.

The three directions perpendicular to the cube faces may be taken as the vertical direction upwards, normal to (001); the horizontal direction, shown by the arrow, normal to (100) and the horizontal direction, normal to (010). Their symmetry axis is the normal to (111), inclined  $54^{\circ}44'$  to each, and this represents the direction of growth of a needle formed under the prescribed conditions. Other symmetry axes corresponding to the vertical direction and horizontal directions with appropriate change of sign are the normals to ( $\bar{1}\bar{1}$ 1), ( $\bar{1}$ 11) and (1 $\bar{1}$ 1).

A set of parallel needles developing side by side may grow together into a lamella or plate whose pole must lie in the great circle constructed around the direction in question as an axis. Thus, around [111] we have the great circle *abc* containing the poles of three planes of form {110} and three of form {112}. Parallel needles coming from the centers of unit cubes whose sides are in contact will grow into plates of the former type, while similar needles coming from a row of cubes whose edges are in contact can form plates of the latter type.

Planes of the former type include two directions of the form [111], as may be seen by constructing the great circle *def* around ( $\bar{1}$ 01) as an axis. In this case needles taking the directions [ $\bar{1}\bar{1}$ 1] and [111] might



in the horizontal and vertical planes defines the plane of this plate and its pole is found in the customary manner at  $P_1$ ,  $90^\circ$  from the great circle along the dotted line perpendicular to the trace in the horizontal plane.  $P_2$ ,  $P_3$  and  $P_4$  are found in the same manner. The angles between these poles, measured with the aid of a stereographic net, are of course the angles sought.

These are all within a few degrees of the theoretical angles between planes of form  $\{112\}$ —*viz.*,  $70^\circ 32'$ ,  $48^\circ 11'$ ,  $60^\circ$ ,  $80^\circ 24'$  and  $33^\circ 33'$ —but do not seem to present a suitable combination of angles for a group of

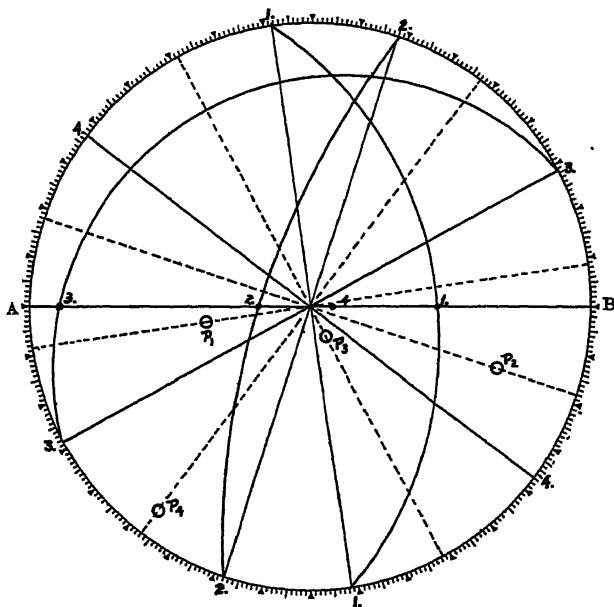


FIG. 2.—DETERMINATION OF ANGLES BETWEEN SEGREGATE PLANES IN BETA BRASS FROM HANEMANN AND SCHRÖDER'S DATA.

our planes of this form. The latter angle was not represented among the families of plates subjected to the above analysis but traces of other plates seem to be evident in the photomicrograph, and it is not improbable that a careful study of all traces to be found in both polished surfaces would give more adaptable data.

Earlier criticism by Mehl and Marzke<sup>3</sup> of a similar treatment of their own data by Phillips<sup>4</sup> to the effect that planes of the form  $\{112\}$  comprise 12 families and should yield that number of traces in a given plane is applicable here. It is possible that a careful examination of Hanemann and Schröder's preparation would yield the required number of traces. According to the hypothesis presented here, however, close-packed atom

<sup>3</sup> Reference of footnote 1, 157.

<sup>4</sup> Reference of footnote 1, 152.

strings representing a  $[111]$  direction may grow together in a preferred direction to form a plane of form  $\{112\}$  and unless they also grow together in two other directions to form the other two planes of form  $\{112\}$  which include this same direction, these planes cannot be formed at all because they do not include any other  $[111]$  direction.<sup>5</sup>

The "perfusion" directions taken to represent the lines of movement of carbon atoms in the face-centered cubic iron lattice are  $[110]$  directions and from these a "perfusion figure" is constructed by joining the 12 points at which these lines drawn from the center of the cube (location of a carbon atom) emerge at the center points of the edges. This figure represents a combination of cube and octahedron and thus has four planes of form  $\{111\}$  and three of form  $\{100\}$  which are held to explain the occurrence of seven sets of traces on certain sections representing the separation of ferrite from austenite or of cementite from austenite, although specific illustrations of such segregate structures are not included.

Referring again to a projection of planes in the isometric system (Fig. 1) it is seen that four primary "perfusion" directions, such as  $[011]$ ,  $[0\bar{1}1]$ ,  $[101]$  and  $[\bar{1}01]$  may have a direction  $[001]$  as an axis of (tetragonal) symmetry; or directions such as  $[101]$ ,  $[110]$ ,  $[\bar{1}01]$  and  $[\bar{1}10]$  may have  $[011]$  as an axis of (binary) symmetry. Three primary "perfusion" directions, such as  $[011]$ ,  $[\bar{1}01]$ , and  $[\bar{1}10]$  have  $[\bar{1}11]$  as an axis of trigonal symmetry. Finally, the angle between two primary "perfusion" directions is bisected by either an  $[001]$  or a  $[112]$  direction.

These general considerations indicate that segregate needles might grow in  $[001]$ ,  $[011]$ ,  $[111]$  or  $[112]$  directions and there appears to be no criterion for choice. It would seem that a so-called "perfusion figure," if it is to represent the planes along which platelike segregation may be considered most probable, should be developed from planes of low indices of which the poles lie in zones around these growth directions taken as axes. On this basis this figure would be a combination of cube, octahedron, dodecahedron and trapezohedron. The forms  $\{122\}$ ,  $\{012\}$ ,  $\{123\}$  and  $\{113\}$  might also be included but experience seems to indicate (Table 1) that such forms are seldom encountered in segregates. From the appearance of photomicrographs of ferrite segregated from austenite, it is certain that the octahedral plane constitutes the preferred plane in the above figure.

Principally through the work of Mehl and his associates, it is now quite evident that segregate phases do not form "in the cleavages"

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<sup>5</sup> It must be admitted that actual proof of plate formation in beta brass along planes of form  $\{112\}$  has not been produced, so that Hanemann and Schröder's mechanism of needle formation by diffusion and a later coalescence into plates may need to be examined in relation to other planes which include the needle direction. Planes of form  $\{110\}$  seem to be excluded on the basis of the data given above and it appears unprofitable at present to discuss other remote possibilities such as  $\{123\}$ .

of the matrix, as often stated in the literature of metallography, nor indeed along the planes of densest atom packing in all cases.

However, it may be seen in the seventh column of Table 1 that the *direction* of a close-packed string of atoms is found in the segregate plane in all cases with the exception of the iron nitride plates in ferrite. It thus appears probable that the transformation habitually starts along one of these directions and that specific cooperative features, such as the approximate matching of planes, determine the grouping of this set of close-packed strings into a segregate plane.

## DISCUSSION

(Arthur Phillips presiding)

C. S. BARRETT, Washington, D. C. (written discussion).—This paper concisely states two objections to the theory of Hanemann and Schröder: (1) the crystal structure of the precipitated phase is a major factor that has not been considered; (2) the mechanism of perfusion fails to predict the geometrical features actually observed in Widmanstätten structures.

Work in a related field adds still another objection, though an indirect and somewhat debatable one, to the suggestion of Hanemann and Schröder. When crystals are grown from solution on the surfaces of other crystals they form in certain instances with a definite mutual orientation. The empirical laws governing this phenomenon of mutual orientation are of considerable importance to the subject at hand, for they are uninfluenced by perfusion, diffusion, strains set up by the new phase, or concentration gradients. The laws governing mutual orientation have been recently stated by Royer<sup>6</sup> and have been verified by more than 80 examples. Mutual orientation occurs only when a lattice plane of one species is identical, within a certain tolerance, with a lattice plane of the other species or with a multiple of this. The relative orientation of the two lattices is such that in the two similar planes in contact the directions having similar parameters in the two lattices are parallel. In cases such as the growth of KCl on NaCl with identical crystal structures and similar parameters, all planes of one resemble corresponding planes of the other; mutual orientation is accordingly observed on all exposed faces. On the other hand, two species having different symmetry but a plane in each species either identical or quasi-identical may mutually orientate themselves with only these planes as conjugate planes. Thus in KI grown on calcite, planes of form (111) in each species are in contact when mutual orientation occurs, similarly plane (111) of KI grows with mutual orientation on the plane (001) of mica.

The similarity between this matching of planes always found in the phenomenon of mutual orientation and the matching of planes generally found in Widmanstätten structures is remarkable. It strongly implies that neither perfusion, diffusion, lattice strains, nor concentration gradients are important in determining either the principal surfaces between matrix and segregate in alloys or the orientation of the segregate lattice with respect to the matrix.

It might be mentioned that in two crystals of the same symmetry and nearly equal parameters mutual orientation occurs with any face whatever as the common

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<sup>6</sup> M. L. Royer: Recherches Expérimentales sur l'Épitaxie ou Orientation Mutuelle de Cristaux d'Espèces Différents. *Bull. Soc. Franc. Minéralogie* (1928) 51, 9-159, 1928,



face; thus many examples are known where neither of the planes growing together contains strings of atoms in closest packing.

R. F. MEHL, Middletown, Ohio (written discussion).—I think it is fair to say that had Hanemann and Schröder used the more elegant stereographic analytical methods they would have avoided a number of pitfalls.

The chief result of the paper by Mathewson and Smith is the fact that the perfusion directions assumed by Hanemann and Schröder cannot account for the Widmanstätten figures observed. The general assumption that perfusion directions, determined only by the lattice structure and type of solid solution, establish uniquely the type of structure obtained may be shown to be impossible from experimental data now available. Much of this has been given in Mathewson and Smith's table, but together with new data might profitably be given here.

In iron-carbon alloys the austenite phase is a solid solution known to be face-centered cubic in structure and known to be interstitial in type, therefore permitting perfusion. On the basis of Hanemann and Schröder's theory, any phase precipitating from austenite should form one and the same Widmanstätten figure. It is now known, however, that ferrite forms (in hypoeutectoid alloys) upon the (111) plane in austenite but that cementite forms (in hypereutectoid alloys) upon some plane or planes, definitely not the (111) plane, symmetrically arranged around the [100] direction in the austenite lattice.

In meteorites, iron-nickel alloys, an austenitic phase, taenite, precipitates on cooling a ferritic phase, kamacite, and the kamacite has been demonstrated by Young, in England, to bear the same crystallographic relationships to the taenite that ferrite bears to austenite in hypoeutectoid steels. The structure formed, the original Widmanstätten figure, is coarse-grained and very well defined. Furthermore, the solid solutions partaking in this precipitation are both substitutional, which should prevent perfusion. We have, then, the fact that there is no crystallographic difference between the Widmanstätten figure formed in steels and that formed in meteorites, though perfusion can be assumed in one case and not in the other. The crystallographic identity of the two structures can be completely explained, of course, by the identity of the crystallographic relationships obtaining in each pair of the participating phases in the two cases.

The work upon which Mr. Marzke reported last year may be cited in a similar way. In this case—the precipitation of the  $\alpha$  and  $\gamma$  phases from the  $\beta$  in the copper-zinc system—perfusion, according to Hanemann and Schröder, is possible but it has been shown that the structures formed when  $\alpha$  precipitates are entirely different from those when  $\gamma$  precipitates, though both form from the same basic lattice.

I should like to digress for a moment from this immediate subject in order to point out that in discussing Widmanstätten figures, and also in discussing age-hardening, it is necessary frequently to refer to the equilibrium curve which in the constitutional diagram delimits the solid solution field. This curve is variously designated as the solid solubility curve, the curve of solubility in the solid state, but has not as yet been given a particular name. It seems strange that when the liquidus and solidus curves were named, this important curve—not then recognized as important, to be sure—escaped christening.

A new term should not be proposed unless it promises to be useful. Furthermore, it should be euphonious, it should be suggestive of the thing it names, and must be, as Mr. Thum points out, of honest linguistic parentage. These requirements seem to be met by the word *solvus*, and might it not be well to name this important curve—the curve of solubility in the solid state—the *solvus curve*?

O. T. MARZKE, Cambridge, Mass.—The work which was reported last year by Dr. Mehl and me<sup>7</sup> on the precipitation of alpha from beta brass is being continued. Many specimens of various compositions and heat treatments have been examined. All our observations indicate that the precipitate, the alpha phase, first comes out in the form of needles. However, there is a tendency for these needles to line up along certain crystallographic planes to give a platelike structure. The formation of such a structure seems to depend on the amount of precipitate, which is determined by the heat treatment and the composition of the alloy. So far neither the direction of these needles nor the planes along which they align themselves have been determined definitely. It seems that if the [111] direction is the direction of the needles, which there is considerable reason to believe is the case, these needles would tend to form plates along planes of which the poles would lie in the great circle around the [111] direction, as the authors suggested, rather than on the {111} planes, as Hanemann and Schröder suggested. In fact, examination of most of our specimens shows conclusively that there are more traces than can be accounted for by planes of the form {111}.

C. H. MATHEWSON (written discussion).—The authors are indebted to Dr. Barrett for drawing attention to recent experimental work revealing a simple geometrical relationship between contacting lattice planes when one substance is allowed to crystallize on the surface of another. The question whether such conditions result in the same cooperative growth features as arise when one substance must originate wholly within another and adjust itself accordingly must be left for future consideration.

Dr. Mehl has reinforced the central ideas of this paper by citing additional evidence contradicting the simple assumption (Hanemann and Schröder) that segregate structures are determined primarily by a process of diffusion prescribed by the crystal-geometry of the matrix phase.

Relative to Dr. Mehl's proposal that the curve of solid solubility be termed "solvus," there can be no doubt that some convenience would result from the introduction of such a simple and expressive term. It may be recalled that the curves of solid solubility delimit a bisolidal region and might appropriately be designated bisolidus curves I and II, according to the prevailing lattice type.

Mr. Marzke has presented additional experimental evidence that alpha separated from beta copper-zinc alloys does not conform in its segregate structure to the "perfusion" rule of Hanemann and Schröder.

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<sup>7</sup> R. F. Mehl and O. T. Marzke: Studies upon the Widmanstätten Structure, II. *Trans. A. I. M. E., Inst. Metals Div.* (1931) 123.

## Seasonal Variation in Rate of Impingement Corrosion

By ALAN MORRIS,\* BRIDGEPORT, CONN.

(Boston Meeting, September, 1931)

IMPINGEMENT attack, as one of the types of corrosion suffered by condenser tubes, has been given a prominent place in corrosion literature of recent years. It has been reproduced and studied in carefully controlled laboratory tests. Much has been learned of its mechanism, and of the effects of variables such as temperature, amount of air, size of bubble and water velocity. Incidentally the technical public has been given comparisons between the behavior of some few metals under various conditions of impingement attack.

The tests recorded here were undertaken in an effort to find at least some sort of qualitative answer to questions which arose occasionally as to the relative resistance of various alloys to impingement attack, and which could not be answered by reference to the literature. The final decision to start work on the problem was influenced in large measure by the nature of the water available in this particular place. The mill of the Bridgeport Brass Co. is located on the Pequonnock River at Bridgeport, Conn., within two miles of its mouth. The water is much like many other estuarine sources which are used in condensers, and which cause particularly severe corrosion. It seemed a most suitable water to use in such tests. As the work progressed an important seasonal variation was noted. The purpose of this note is to record this seasonal effect. The results of individual tests are given only incidentally.

### IMPINGEMENT TESTS

Early in 1929 the apparatus was built. The samples were disks of 1-in. dia., cut from sheet metal. They were cleaned with fine emery cloth and set in holders, as shown in Fig. 1.

A stream of water pumped directly from the river impinged on the surface of the sample. Compressed air was injected into the water stream through an air duct. Water pressure was maintained at about 35 lb. per sq. in. and air was controlled by a needle valve. Velocity of

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\*Research Engineer, Bridgeport Brass Co.

jet was 25 ft. per sec. Basically, the test is similar to those described by Bengough, May and Pirret<sup>1</sup> and by May.<sup>2</sup>

It was realized that this was not really a carefully controlled laboratory test. The apparatus was made of metal and not of rubber, though the samples were held between two rubber washers. The water temperature would vary seasonally. While we could control the amount of air we could not vary the bubble size. But it was felt that the conditions more nearly approximated those of some cases of condenser tube service than if pure sea water or synthetic salt water were used.

The choice of alloys tested was not made as the result of a thoughtfully laid out program but represents a series of comparisons of various metals which, for one reason or another, happened to be of momentary interest. It could only be hoped to compare two metals as to their resistance to impingement attack by running as many samples of each

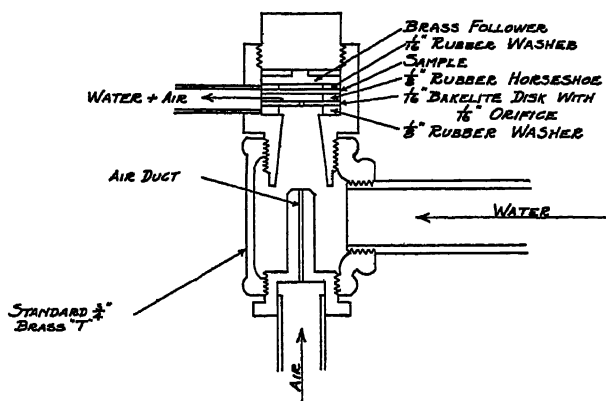


FIG. 1.—DESIGN OF JET.

as possible *at the same time* and averaging the results of the individual tests. Accordingly the apparatus was made to accommodate 20 samples, or 10 of each of the two metals being compared (Fig. 2). Brass pipes, 2-in. and 3-in. dia., capped at the ends, served as air and water distributors, respectively. These were placed horizontally and each had 10 outlets on each side leading to the jets. Samples of the metals were placed in alternate holders, so as to offset possible variation in distribution of water and air.

After the test, a scale varying in color from brown to black covered the samples, except for the spot where the jet impinged. That spot was

<sup>1</sup> G. D. Bengough, R. May and R. Pirret: The Causes of Rapid Corrosion of Condenser Tubes. *Trans. North East Coast Institution of Engineers and Shipbuilders* (1923-1924) 40, 23.

<sup>2</sup> R. May: Eighth Report to the Corrosion Research Committee of the Institute of Metals. *Jnl. Inst. Metals* (1928) 40, 141.

generally bright and clean, with a sharply defined, almost circular depression about  $\frac{1}{8}$  in. across. The depth of the depression was used as a measure of attack. The samples were carefully measured before and after exposure, the difference being expressed in mils penetration per 100 hr. of test.

The first test was started May 17, 1929. The first two comparisons so made gave results of about 1 mil per 100 hr., which is about of the same order of magnitude as the results given by Bengough, May and Pirret. The third test, which ran from June 17 to 22, 1929, gave results three times as great. The fourth test was run from June 24 to 29, comparing

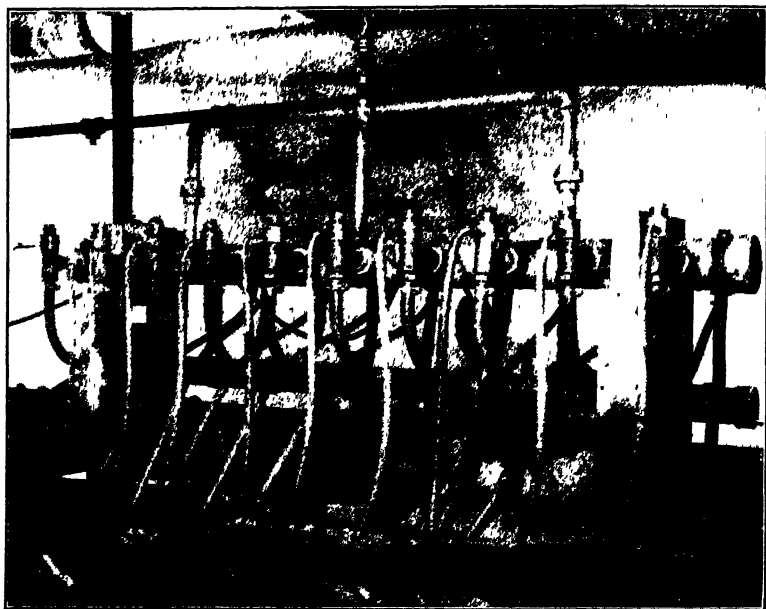


FIG. 2.—APPARATUS USED IN IMPINGEMENT TESTS.

the same alloys as test No. 3. When the samples were removed 19 of the 20 had been pierced cleanly through and holes had been made in the brass screw plugs which held them in place. The samples were 10 mils thick and the test had run 119 hr. The rate of attack had increased at least tenfold between June 5 and 29. From that time on samples 0.050 in. thick were used.

This experience was duplicated in the summer of 1930 and again in 1931. In all three years the increased corrosion was coincident with the period when the water gave off that unpleasant odor which is characteristic of such waters in warm weather. At the same time the external surfaces of the brass parts of the apparatus became covered with a black film. Qualitative test of the water showed hydrogen sulfide.

In his discussion of Dr. Bengough's paper,<sup>3</sup> P. C. Parker, of the Newcastle-upon-Tyne Electric Supply Co., reported:

Scale corrosion at the inlet ends has been very marked, but the pitting of condenser tubes has been the outstanding feature. For example, of new 70:30 brass or copper tubes put in commission in June, 40 per cent may be pitted inside a month, but if these same tubes were put into commission in November, only a few might be pitted at the end of the year, and, during the next year, perhaps only one per cent would fail.

. . . It was ultimately found that the dissolved gases in the water were the main factors in tracing the seasonal effect of tube pitting. Starting in November, it was found that the dissolved oxygen was of much higher content than dissolved carbon dioxide, and we certainly obtained a natural protecting scale which forms rapidly

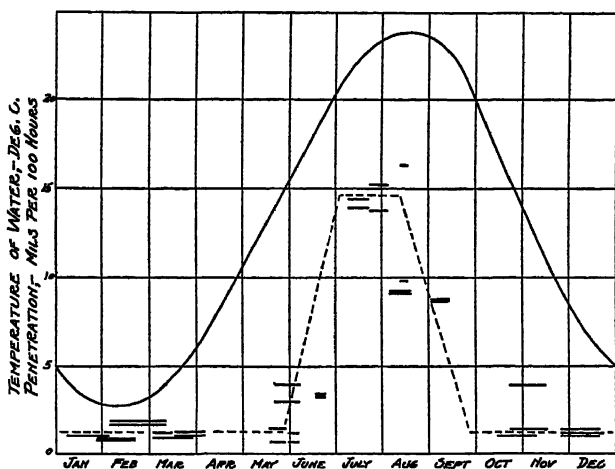


FIG. 3.—RESULTS OF TESTS AND WATER-TEMPERATURE READINGS.

Smooth curve indicates mean water temperature.

Short horizontal lines represent results of individual tests, both magnitude and duration.

Dotted line gives approximate trend of results.

during part of October and November, and less so up to March. In the month of March the dissolved carbon dioxide in Tyne water becomes about equal to the dissolved oxygen content, and later, the dissolved carbon dioxide increases considerably above the dissolved oxygen. Our assumption has been that the dissolved carbon dioxide, which is in excess in the summer months, destroys the protective scale, the serious pitting starting again somewhere about July, and in a dry autumn may continue until October; this effect is repeated yearly.

Frequent water-temperature readings have been made throughout the two years during which the tests reported in the present paper have been running. When these were plotted it was found that the temperature curves for the two years practically coincided. The scatter of individual readings was within  $\pm 1^\circ \text{C}$ . This scatter is partly accounted

<sup>3</sup> G. D. Bengough, R. May and R. Pirret: *Op. cit.*

for by the observed fact that the temperature drops about 1° C. as the tide changes from low to high and vice versa—rises as the tide falls.

Fig. 3 is a plot of all results obtained in 1929, 1930 and 1931, the years superimposed. The marked increase in rate of attack during the summer months is clearly indicated. The seasonal variation shown is greater than the difference between any pair of metals tested. It seems probable that the marked increase in rate of attack during the heat of summer is in part a direct result of increase in water temperature. According to Mr. Parker, the nature and quantities of dissolved gases are responsible in large measure. Another possible contributing factor, as mentioned by Bengough and May<sup>4</sup> is the presence of fermentation products of micro-organisms. No series of water analyses has been undertaken, but it is hoped that such data may be gathered at a later date. Table 1 gives the analyses of all alloys tested and Table 2 shows the results of all tests plotted in Fig. 3.

TABLE 1.—*Analyses of Alloys Tested*

Alloy	Cu, Per Cent	Sn, Per Cent	Pb, Per Cent	Fe, Per Cent	Si, Per Cent	Al, Per Cent	Ni, Per Cent	P, Per Cent	Zn, Per Cent
Admiralty 1.....	70.71	1.01	0.01	0.01					Rem.
Admiralty 2.....	71.13	1.12	0.035	0.02					Rem.
Admiralty 3.....									
(8 numbers hard).....	70.10	1.08	0.023	0.014					Rem.
Aluminum brass.....	75.41			0.03		2.02			Rem.
85-15.....	85.44		0.01	0.02					Rem.
Munts 1.....	61.18		0.33	0.02					Rem.
Munts 2.....	61.89		0.29	0.02					Rem.
High brass 1.....	66.41		0.52	0.02					Rem.
High brass 2.....	65.91		0.52	0.01					Rem.
Naval brass.....	60.40	0.55	0.043	0.03					Rem.
Silicon tin.....									
Bronze.....	Rem.	1.71		0.017	0.97				
Al-Si bronze 1.....	97.01			0.09	1.24	1.84			
Al-Si bronze 2.....	90.91			0.02	3.02	6.10			
Al-Si bronze 3.....	92.45			0.02	1.61	5.88			
5 per cent nickel silver.....	68.00		0.06	0.06	Mn 0.05		5.64		
10 per cent nickel silver.....	64.34			0.13	Mn 0.03		9.10		
18 per cent nickel silver.....	64.80			0.11	Mn 0.06		17.88		
Phosphor copper.....								0.016	

The results of individual comparisons, as listed in Table 2, must not be given too general an interpretation. They represent the relative susceptibility of the various pairs of alloys to impingement attack only under the special conditions of these tests.

As in all corrosion investigations, a certain scatter of results in any given run has been experienced. It has been convenient to plot the

<sup>4</sup> G. D. Bengough and R. May: Notes on the Corrosion and Protection of Condenser Tubes. Pamphlet issued by Inst. of Metals (1925).

TABLE 2.—*Results of Tests Plotted in Fig. 3*

Run	Alloy	Dates of Test	Penetration per 100 Hr., Mils	Mean Water Temperature, Deg. C.
1	Admiralty 1 Aluminum brass	5-17-29 to 5-27-29	0 7 1.5	14.0
2	Admiralty 1 85-15	5-28-29 to 6-5-29	0 7 1 1	15.5
3	Munts 1 High brass 1	6-17-29 to 6-22-29	3 3 3.2	18.5
4	Munts 1 High brass 1	6-24-29 to 6-29-29	Samples 0 010 in thick all pierced except 1	19.5
6	Munts 2 High brass 2	7-8-29 to 7-20-29	14.4 13.9	21.5
7	Munts 2 High brass 2	7-22-29 to 8-3-29	13.8 15.2	23.2
8	Munts 2 High brass 2	8-5-29 to 8-17-29	9.2 9.1	23.8
10	Munts 2 Naval brass	10-14-29 to 11-9-29	0.9 0.9	14.2
11	Admiralty 2 Si-Sn bronze	11-25-29 to 12-21-29	1.1 1 2	7.1
12	Admiralty 2 Si-Sn bronze	1-7-30 to 2-4-30	1 1 1 0	3.3
13	Munts 2 Naval brass	2-5-30 to 3-10-30	1 9 1.6	2.9
14	Admiralty 2 Admiralty 3 (hard)	3-17-30 to 4-5-30	1.0 1.2	5.5
16	Admiralty 2 Al-Si bronze 1	8-12-30 to 8-16-30	16.3 9.8	23.8
17	Admiralty 2 Al-Si bronze 2	9-2-30 to 9-13-30	8.7 8.6	23.0
18	Admiralty 2 Al-Si bronze 3	10-22-30 to 11-15-30	1.4 3.9	12.8
20	Admiralty 2 5 per cent nickel silver	11-25-30 to 12-20-30	1.4 0.9	7.35
21	Admiralty 2 10 per cent nickel silver	1-20-31 to 2-21-31	0.9 0 75	2.8
22	Admiralty 2 18 per cent nickel silver	3-2-31 to 3-28-31	1.2 0.9	4.6
24	Admiralty 2 Phosphor copper	5-19-31 to 6-6-31	3.9 3.0	15.



results on Hazen arithmetic probability paper, as described by Passano and Hayes.<sup>5</sup> If data are of such a nature as to give a probability curve when plotted on Cartesian coordinate paper, they may be expressed in terms of cumulative percentages and plotted on Hazen paper as a straight line. Although 10 determinations might be considered too few upon which to base a probability curve, the method has been an aid in studying the results of these tests.

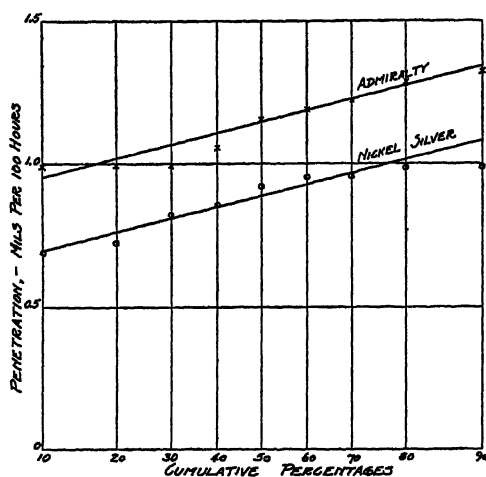


FIG. 4.—RESULTS OF RUN 22 PLOTTED ON HAZEN PAPER.

Fig. 4 shows the plot corresponding to run 22, in which regular Admiralty metal was compared with 18.0 per cent nickel silver. The points indicate the positions of the straight lines fairly closely. It can be seen at a glance:

1. That the scatter is about the same for each metal, since the lines are about parallel.
2. That the least deeply attacked Admiralty samples have suffered to about the same extent as the most deeply attacked nickel-silver samples.
3. That the most expectable rates of attack for Admiralty metal and for nickel silver under the conditions of this test are 1.2 and 0.9 mils per 100 hr., respectively. These are the points where the straight lines cross the 50.0 per cent ordinate.

## DISCUSSION

(E. M. Wise presiding)

J. R. FREEMAN, JR., Waterbury, Conn.—This paper has considerable practical value because estuarine water was used, taken directly from the river. The data,

<sup>5</sup> R. F. Passano and A. Hayes: A Method of Treating Data on the Lives of Ferrous Materials. *Proc. Amer. Soc. Test. Mat.* (1929) 29, Pt. 2, 220.

therefore, are free from the objection of the use of synthetic waters prepared in the laboratory.

I would like to ask Mr. Morris whether he has considered the relation between flow of the river to the rate of impingement attack.

In connection with the temperature effect, Mr. Morris mentioned the possible associated effects of carbon dioxide, sulfur dioxide and organic matter in the water but not the possible variations in the salt content of the water, which one would expect to occur with various stages of flow of the river from season to season. I would like to know whether any such data are available.

E. M. WISE, Bayonne, N. J.—There are two factors that may have some small bearing on this subject. The whole behavior appears to be tied up with the failure to form a protective film. For this reason it is particularly interesting, particularly in light of the results of the English experiments in which the time of initiating a condenser group into service exercises a marked influence upon its subsequent life.

It would seem that an investigation of methods for developing a proper film on new tubes would be profitable and so that means might be devised for preconditioning tubes, which are to be installed at the wrong time of the year.

In regard to the possible factors governing this seasonal variation, perhaps the amount of abrasive material in the water—that is, suspended sand or silica, things of that sort—might enter in; and, further, the seasonal changes may cause a change in the acidity, that is the pH of the water. Is there any evidence of that? I am thinking of the pH primarily because that integrates much of the  $\text{CO}_2$ .

A. MORRIS (written discussion).—In answer to Mr. Freeman's question as to the possible effect of dilution due to seasonal changes in flow of the river, it may be said that the dilution is probably slight. The influx of fresh water is relatively small at any season. However, no data are available as to possible seasonal variation in salt content.

Run 14, comparing the cold-worked with annealed Admiralty metal, was made with the idea of determining, if possible, whether mechanical abrasion by small hard particles in the water stream played a part, as suggested by Mr. Wise. Apparently there was little difference between attack on the hard and soft material. It might also be noted in this connection that on various occasions when the air duct had been plugged so that no air entered the water stream, the attack was negligible. Therefore it would seem that mechanical abrasion by suspended matter was a minor factor in these particular tests, if indeed it was a factor at all. No pH determinations have been made.

## Influence of Stress on Corrosion\*

By D. J. McADAM, JR.,† WASHINGTON, D. C.

(Boston Meeting, September, 1931)

### PART I.—OUTLINE OF INVESTIGATION, DESCRIPTION OF METHODS AND MATERIAL

#### *Previous Investigation of the Influence of Stress on Corrosion*

IN 1917 Haigh<sup>1</sup> presented evidence that under simultaneous corrosion and cyclic stress metals may fail at lower stresses than if the corrosion is prior to the cyclic stress. In 1926 the author, while investigating the cooling effect of water on the fatigue resistance of metals, found that under these conditions steel specimens fail at stresses far below the endurance limit.<sup>2</sup> (By "endurance limit" is here meant the fatigue limit obtained with specimens as free as possible from stress concentration and corrosive influences.) This led to an investigation (at the Naval Engineering Experiment Station, Annapolis, Md.) of the influence of cyclic stress on corrosion.

This investigation may be divided into three parts. The first part was a general survey of the conditions necessary to cause complete failure under corrosion and cyclic stress of relatively high frequency. The entire process by which metals fail under these conditions was called "corrosion-fatigue." "Corrosion-fatigue limits" for a large number of metals were determined and the relationships of these limits to chemical composition, heat treatment and physical properties were established. The conclusion was reached that corrosion-fatigue is due to the accelerating influence of cyclic stress on corrosion. Results of this part of the investigation were presented in five papers.<sup>3-6</sup>

The second part of the investigation was a preliminary study of the influence of cyclic stress on corrosion. Each experiment was conducted in two stages. The first was a corrosion stage in which the specimen was corroded under cyclic stress; the second was a fatigue stage, in which the previously corroded specimen was tested (without further corrosion) to determine its fatigue limit. The difference between this fatigue limit and the endurance limit was used as a criterion of the "damage" due to

\* The experiments described in this paper were made at the Naval Engineering Experiment Station, Annapolis, Md. The diagrams were drawn and the paper was written after the transfer of the author to the U. S. Bureau of Standards.

† Metallurgist, U. S. Bureau of Standards.

<sup>1</sup> References are on page 24.

the corrosion. In this preliminary investigation by means of two-stage experiments, the stresses used in the first stage (corrosion stresses) were no higher than the corrosion-fatigue limit. Results obtained in this part of the investigation were presented in two papers.<sup>7,8</sup>

In the third part, the field of investigation was extended to include corrosion stresses higher than the corrosion-fatigue limit, and recently it was found possible<sup>12,13</sup> to use (nominal) corrosion stresses higher than the endurance limit. The use of the higher corrosion stresses has made it possible to investigate the effect of very low cycle frequencies. Considerable information has thus been obtained about the influence of stress range and cycle frequency on corrosion. The conclusion has been reached that corrosion under cyclic stress differs only in degree from ordinary stressless corrosion. Pits formed under corrosion and cyclic stress are sharper and deeper than pits formed in the same time under stressless corrosion. Cyclic stress accelerates corrosion, and the resultant corrosion pitting (through stress concentration at the bottoms of the pits) increases the actual stress. Corrosion under the influence of cyclic stress has been called "fatigue corrosion"<sup>12</sup> with the understanding that the name does not imply that the process is related to ordinary fatigue. Results of this part of the investigation have been presented in five papers.<sup>9-13</sup>

#### *Outline of Continued Investigation of Influence of Stress on Corrosion*

*Object and Method.*—The object of the investigation described in this paper was to study further the influence of stress range and cycle frequency on corrosion. For this purpose some alloys that have not been studied previously were included in the investigation.

The method of experiment was that described in previous papers.<sup>7-13</sup> Each experiment was in two stages. In the first stage each specimen was subjected to cyclic stress while in contact with water. In the second stage the specimen, after being oiled, was subjected to fatigue test at 1450 r.p.m. in air.

*Corrosion Stage.*—In the corrosion stage, the specimens were corroded in a water stream, which was applied diagonally so as to surround the stressed surface entirely with water. Specimens were corroded under various stresses, at various cycle frequencies, and for various times. The specimens were then rinsed with alcohol, dried and covered with a heavy mineral oil. In most of these experiments, a calcium carbonate water was used. The composition of this water was given in a previous paper.<sup>3</sup> In some experiments, Severn River water was used. The salt content of this water is about one-sixth that of sea water.

*Resultant Fatigue Limits and Their Relationship to Three Other Variables.*—In the second stage, each specimen was subjected to fatigue test. An estimate was then made of its probable fatigue limit. For each

specimen, therefore, the two-stage experiment establishes four variables. The four variables are corrosion stress, time and number of cycles in the corrosion stage, and resultant fatigue limit. Relationships between these four variables were represented in previous papers<sup>9-13</sup> by diagrams of various types. In the present paper, three of these types (Types 5, 10 and 11a) will be considered.

### *Machines and Specimens*

The rotating-cantilever machines and specimens have been described in previous papers.<sup>14,15</sup> Rotating-cantilever machines for testing specimens at 10,000 r.p.m. have been described in recent papers.<sup>11,12</sup>

The conically tapered specimen is so designed that the maximum stress is  $\frac{3}{4}$  in. out from the inner fillet, and the stress varies only about 1.5 per cent. over a length of about  $1\frac{1}{2}$  in. With this specimen, a comparatively large region may be subjected to fatigue-corrosion.

The method of longitudinal and transverse polishing of specimens has been previously described.<sup>14,15</sup> The surface finish by this method is sufficiently smooth to permit examination of the structure at a magnification of 100.

### *Material, Chemical Composition and Heat Treatment*

Material for the investigation was obtained in the form of round rods 1 in. in diameter. Chemical compositions are given in Table 1. Details of heat treatment are given in Table 2.

### *Tension and Impact Tests*

Results of tension and Charpy impact tests are given in Table 3. In this table, "elastic limit" means the highest stress that leaves no appreciable permanent deformation after removal of the load. "Proof stress" means the stress that results in permanent deformation of 0.0001 in. per inch of gage length, after removal of the load.

## PART II.—INFLUENCE OF CYCLIC STRESS ON CORROSION, AS ILLUSTRATED BY TYPE 5 DIAGRAMS

### *General Description of Type 5 Diagrams*

The simplest diagram to illustrate the influence of cyclic stress on corrosion is the type 5 diagram. Type 5 diagrams were presented and discussed in five previous papers.<sup>9-13</sup> The influence of cyclic stress on corrosion is illustrated better by diagrams of other types, derived from type 5 diagrams. Nevertheless, type 5 diagrams themselves illustrate important relationships between the four variables, corrosion-stress, time, number of cycles and resultant damage.

TABLE 1.—*Chemical Composition of Material*  
All Values Are Averages of at Least Two Determinations, Usually More

Alloy	Designation	Constituents, Per Cent.												
		Carbon	Manganese	Phosphorus	Sulfur	Silicon	Nickel	Chromium	Vanadium	Copper	Iron	Aluminum	Lead	Zinc
Chromium-nickel steel.....	BW	0.39	0.57	0.018	0.017	0.19	1.83	0.92						
Chromium-vanadium steel..	AU	0.34	0.71	0.016	0.022	0.21		1.05	0.16					
Stainless iron .....	JB	0.11	0.41	0.012	0.026	0.11	0.43	12.71		0.06				
Nickel, cold rolled.....	EO	0.098	0.03	0.006	0.011	0.09	98.96*			0.17	0.57			
Nickel, cold drawn.....	IT	0.085	0.08	0.003		0.09	99.17*			0.16	0.42			
Aluminum bronze.....	KE									90.39	0.17	10.00	None detected	
Aluminum bronze.....	KF									87.69	2.04	10.50		
Copper-nickel-silicon alloy..	KBA-8		None			0.82	3.27			96.96	0.087			
Muntz metal.....	J									60.48			0.10	39.38
Nitalloy .....	KC	0.36	0.57	0.019	0.010	0.31	0.10	1.62				2.03		

\* Obtained by difference.

TABLE 2.—Heat Treatments of Material

Alloy	Designation	Temp. Heated, Deg. F.	Time Held, Min.	Cooled in	Temp. Reheated, Deg. F.	Time Held, Min.	Cooled in
Chromium-nickel steel.....	BW-W-10	1550	60	Water	1000	120	Furnace
Chromium-vanadium steel.....	AU-O-10	1575 <sup>a</sup>	60	Oil	1000	60	Furnace
Stainless iron.....	JB-W-12	1800	60	Water	1200	120	Furnace
Nickel, cold rolled.....	EO-6	600	120	Furnace			
Nickel, cold drawn.....	YT-6	600	120	Furnace			
Aluminum bronze.....	KE-6	600	180	Furnace			
Aluminum bronze.....	KF-6	600	180	Furnace			
Copper-nickel-silicon alloy.....	KBA-8 <sup>b</sup>	As received					
Muntz metal (rolled).....	J	As received					
Nitalloy <sup>c</sup> .....	KC-O-12	1750	60	Oil	1200	280	Furnace

<sup>a</sup> Previously heated to 1700° F., held 60 min. and cooled in air.<sup>b</sup> Hard-drawn rods heat treated. Final treatment, 2 hr. at 425° C.<sup>c</sup> Heat treated and machined at Annapolis. Then given nitride treatment by manufacturers.

In the present paper, type 5 diagrams are shown in Figs. 1 to 6, which, with the exception of the diagrams in Fig. 4, represent alloys that have not been so represented previously. In Fig. 4 are shown diagrams representing an alloy that has been discussed in previous papers.<sup>10,11</sup> The diagrams in Fig. 4 have been redrawn, however, to include results of additional experiments.

Each graph in Figs. 1 to 6 represents the relationship between corrosion time and resultant fatigue limit for a chosen stress and cycle frequency. Each series of graphs represents some one cycle frequency. Comparison of the graphs of any series, therefore, gives information about the effect of corrosion-stress. Each experimental point represents the result obtained with a single specimen. The method of obtaining resultant fatigue limits by extrapolation of stress-cycle graphs has been illustrated and described in previous papers.<sup>7,8</sup> To save space, stress-cycle graphs have not been included in this paper.

All the graphs of a series have a common origin. The ordinate of this common origin represents the endurance limit of the metal (as obtained by test of uncorroded specimens). The course of each graph illustrates the decrease in resultant fatigue limit with increase in corrosion time. The uppermost graph of each series represents the effect of stressless corrosion. The other graphs represent the damaging effect of corrosion under the indicated cyclic stress.

### *Total Damage and Net Damage*

Total damage and net damage have been discussed in five previous papers.<sup>9-13</sup> The total damage due to corrosion under cyclic stress is measured by the distance of the type 5 graph (at any point) below a horizontal line through the origin of the graph. This damage, however, is not due entirely to cyclic stress. The effect of the cyclic stress is measured by the vertical distance of the type 5 graph (at any point) below the stressless-corrosion graph. The net damage, therefore, is the total damage less the damage that would be caused in the same time by stressless corrosion. The influence of cyclic stress is measured by net damage rather than by total damage.

### *Type 5 Diagrams, Nickel, Aluminum Bronze and Stainless Iron*

Type 5 diagrams for nickel, aluminum bronze and stainless iron are shown in Figs. 1 to 4. The graphs in these figures resemble the type 5 graphs for monel metal and stainless iron presented in previous papers.<sup>11-13</sup> Because of their downward curvature, these graphs have been called "accelerated damage" graphs. The stressless-corrosion graphs for nickel and for monel metal curve downward only slightly unless they are extended to abscissas representing more than 100 days.



For stainless iron, the downward curvature is slight unless the graph is extended beyond 200 days. Beyond about 240 days, however, the downward curvature increases rapidly. The influence of cyclic stress on corrosion of all these alloys will be discussed in Parts III and IV in connection with derived diagrams.

*Type 5 Diagrams, Chromium-nickel Steel in Carbonate Water and in Severn River Water*

Figs. 5 and 6 show results of some preliminary experiments made primarily to investigate the influence of various corrosion conditions on the form and position of derived diagrams to be discussed in Parts III and IV. Fig. 5 shows type 5 diagrams representing the behavior of chromium-nickel steel in carbonate water and in Severn River water. The graphs in these diagrams, like the graphs for carbon steels and ordinary alloy steels in previous papers,<sup>9-13</sup> are retarded-damage graphs.

*Effect of Reducing the Supply of Oxygen*

To investigate roughly the effect of reducing the supply of oxygen, some experiments were made with specimens covered with cotton and then subjected to a water stream as usual. The cotton was applied to each specimen in layers of approximately the same thickness. The ends of the applied layer were then covered with impervious material, so that all the water that reached the specimen must diffuse through the layer of cotton. The rate of oxygen supply, therefore, depended on the rate of diffusion through the cotton. Consequently, the corrosion conditions at the surface of the specimen were similar to the conditions at the surface of a rather deeply submerged specimen. This rough method was adopted to obtain some information about the subject in absence of time and opportunity to develop a more refined method.

Results obtained under these conditions are shown in Fig. 6. Comparison is made in this figure between the stressless-corrosion graph representing cotton-covered specimens and the graph representing uncovered specimens. The initial rate of damage, as indicated by the slope of the graph, is much less for cotton-covered specimens than for uncovered specimens. Under either corrosion condition, the rate of damage gradually decreases and finally becomes very slow. When this almost negligible rate is reached, however, the total damage is much less for cotton-covered than for uncovered specimens. The influence of cyclic stress will be discussed in Parts III and IV, in connection with the derived diagrams.

*Effect of Coating Specimens with Red Lead*

Fig. 6 also shows results of fatigue-corrosion of specimens that had received two coats of red lead. All these specimens were tested to com-

plete failure in the first or corrosion stage. The form of the type 5 graphs for specimens coated with red lead, therefore, is not known. It seems probable, however, that these graphs, like the graphs for corrosion-resisting steels, are accelerated-damage graphs. The influence of the red-lead coating on the form and position of the derived graphs will be discussed in Part IV.

### *Constant Net Damage*

By "constant net damage" is meant constant (percentage) lowering of the fatigue limit below the fatigue limit that would result (in the same time) from stressless corrosion. To derive a constant net-damage diagram from a type 5 diagram a line may be drawn below the stressless-corrosion graph so that the ordinate of every point in the line is a constant percentage of the corresponding ordinate of the stressless-corrosion graph. The broken lines in Figs. 1 to 6 have been so drawn. The coordinates of the intersections of these lines with the fatigue-corrosion graphs are used in plotting the constant net-damage graphs.

Various types of constant net-damage diagrams may thus be obtained. Two types, however, have been found most useful. These are types 10 and 11a, which have been discussed in previous papers.<sup>9-15</sup> Type 10 diagrams will be discussed in Parts III and IV. Type 11a diagrams will be discussed in Part V.

## PART III.—INFLUENCE OF CYCLE FREQUENCY ON CORROSION

### *General Description of Type 10 Diagram*

The type 10 diagram and the type 11a diagram may be considered as two views of a three-dimensional diagram. Neither type of two-dimensional diagram can be studied thoroughly without giving some consideration to the other type. Attention will first be confined, however, to the type 10 diagram.

A type 10 graph is a constant-stress graph illustrating the relationship between the total number of cycles and the corrosion time necessary to cause constant net damage. The time necessary to cause constant net damage, however, varies inversely as the average rate of net damage. Hence abscissas in a type 10 diagram represent, according to the direction in which they are measured, either corrosion times or rates of net damage. In a type 10 diagram plotted with logarithmic coordinates (as illustrated by the diagrams in Figs. 7 to 13), constant-frequency lines are diagonal and parallel. A type 10 diagram, therefore, shows the influence of cycle frequency on the time necessary to cause constant net damage, and on the rate of net damage.

In discussing the type 10 diagrams the direction of measurement of abscissas will be viewed as horizontal and the direction of measurement

of ordinates will be viewed as vertical. It should be noted that this use of the words "horizontal" and "vertical" is not appropriate when a type 10 diagram is studied as the plan or top view of a three-dimensional diagram. When a type 10 diagram is studied thus, both coordinates should be considered as horizontal, and a stress coordinate (perpendicular to the plane of the type 10 diagram) should be considered as vertical. In the present paper, however, type 10 diagrams will be discussed as two-dimensional diagrams.

### *Influence of Cycle Frequency on Corrosion of Nickel*

Figs. 7 and 9 show type 10 diagrams representing two samples of nickel. The sample represented in Fig. 7 was commercial cold-drawn nickel. The sample represented in Fig. 9 was a cold-rolled sample having much higher tensile strength and elastic limit. It was part of a lot that had been used in previous investigations.<sup>4,5</sup>

To the right of the 50 r.p.m. line in Figs. 7 and 9 the graphs are nearly horizontal. As they extend to the left of this line, the graphs (except the graphs in Fig. 7 representing stresses higher than the endurance limit), curve abruptly upward, and at high frequencies evidently become nearly vertical. The downward curvature of some of the high-stress graphs in Fig. 7, at the high-frequency ends, is probably due to thermal effects.

The type 10 graphs for nickel resemble in form the type 10 graphs for steels and aluminum alloys shown in previous papers.<sup>11-13</sup> The graphs for steels, aluminum alloys, and nickel differ chiefly in the cycle frequency at which abrupt upward curvature begins. In this respect, nickel is intermediate between steels and aluminum alloys.

Type 10 graphs for monel metal, as shown in previous papers,<sup>12,13</sup> differ considerably in form from type 10 graphs for steels and aluminum alloys. The graphs for monel metal, as they extend to the right from the high-frequency end, first curve toward the horizontal then reverse their curvature and turn downward. At the low-frequency end, they become practically vertical. The graphs for steels, aluminum alloys and nickel show no clear evidence of downward curvature, though they have been extended to frequencies as low as 5 cycles per hour. The graphs for steels would probably curve downward and become practically vertical, if extended to still lower frequencies. Evidence for this, as presented in a previous paper,<sup>13</sup> is based chiefly on cases of severe pitting or complete failure of boilers in service. It is possible, also, that the graphs for aluminum alloys and nickel may curve downward, if extended to sufficiently low frequencies. These conclusions apply to diagrams obtained with specimens corroded in carbonate water. It will be shown later that the form of the type 10 graph is influenced considerably by variation in the corrosion conditions.

*Influence of Cycle Frequency on Corrosion of Aluminum Bronze*

Figs. 8 and 13 show type 10 diagrams representing two samples of aluminum bronze differing considerably in chemical composition. The diagram in Fig. 8, representing the stronger sample, covers a range of cycle frequency from 10,000 cycles per minute to 1 cycle per day.

The graphs in Fig. 8 are drawn to represent the most probable position and interrelationship. The steeply sloping, low-frequency ends of the graphs, especially the broken-line extensions, can be considered only approximately correct. More experiments would be needed to determine exactly the type 5 stressless-corrosion graph and the fatigue-corrosion graphs (in Fig. 3), from which the diagram in Fig. 8 is derived. Nevertheless, it should be noted that even relatively large changes in the type 5 graphs would cause only slight changes in the derived graphs, which are plotted on a logarithmic scale. The diagram in Fig. 8, therefore, may be considered approximately correct.

The type 10 graphs for aluminum bronze differ greatly in form from the type 10 graphs for steels, aluminum alloys and nickel. The graphs for aluminum bronze resemble in form the graphs for monel metal presented in previous papers.<sup>12,13</sup> As they extend to the right, the graphs for aluminum bronze curve downward and become practically vertical. As they extend to the left, the graphs (with the exception of the 25,000 and 20,000 graphs in Fig. 8) show no tendency to curve upward. This is due probably to the fact that, with the two exceptions, the graphs represent corrosion stresses higher than the endurance limit. The 25,000 and 20,000 graphs in Fig. 8 evidently curve upward, at the high-frequency end, as do the graphs for nickel in Fig. 7 and the graphs for steels, aluminum alloys and monel metal shown in previous papers.<sup>11-13</sup>

It is assumed, though not proved, that the approach to the vertical direction, shown by the graphs in Fig. 8, continues until the graphs reach the horizontal line B, the ordinate of which represents 0.5 cycle. Below this line, the graphs would probably curve abruptly to the right. For practical purposes, line B may be considered the lower boundary of the type 10 diagram.

The half cycles, represented by points in line B, evidently involve harmonic variation of stress between a compressive and an equal tensile value. Steady tensile stress, however, may be viewed as a half cycle of stress that increases rapidly from zero to a maximum and is then maintained at the maximum for a relatively long time. At present there is no experimental evidence to permit a comparison of the effect of this inharmonic cycle with the effect of the harmonic cycle represented by the graphs in Fig. 8. Type 10 graphs obtained with the inharmonic cycle described, however, would probably be similar in form to the graphs in Fig. 8. The graphs in Figs. 8 and 13, therefore, illustrate qualitatively

the relative influence of cyclic stress and steady stress on corrosion. As indicated by the nearly vertical portions of these graphs, corrosion of aluminum bronze in carbonate water is considerably influenced by steady stress.

### *Influence of Cycle Frequency on Corrosion of Stainless Iron*

Fig. 9 shows a type 10 diagram for "stainless iron." A type 10 diagram for the same sample of stainless iron was shown in a previous paper.<sup>11</sup> The diagram in the present paper, however, has been redrawn on the basis of the greater number of data now available.

The scatter of results obtained with corrosion-resisting steels is greater than the scatter obtained with any other alloys that have been investigated. Because of this wide scatter, the results must be interpreted largely in the light of information obtained with other alloys. The interpretative graphs in Fig. 9 have been drawn so as to represent the most probable relationship for the diagram as a whole, taking into account also the relationship between this diagram and the corresponding type 11a diagram shown in Fig. 14.

In the type 10 diagrams for corrosion-resisting steels, presented in a previous paper,<sup>11</sup> no definite interpretative graphs were drawn. Broken lines sloping slightly to the right, however, were drawn to illustrate the general trend rather than the form of the graphs. In Fig. 9 of the present paper, curved interpretative graphs have been drawn to represent the most probable form of the ideal diagram. At intermediate frequencies, these graphs are nearly horizontal, as are the graphs for ordinary steels. As they extend to the left, the graphs (except those representing stresses near or above the endurance limit) curve upward, as do the graphs for ordinary steels. As they extend into the low-frequency end of the diagram, the graphs probably begin to curve downward near the 10 r.p.m. line. The downward curvature probably increases rapidly (especially for the high-stress graphs) until the graphs become practically vertical.

The available evidence, therefore, indicates that the ideal type 10 graphs for stainless iron resemble the type 10 graphs for ordinary steels. The downward curvature of the graphs, however, probably begins at somewhat higher frequencies for stainless iron than for ordinary steels.

### *Influence of Cycle Frequency on Corrosion of Nitrided Steel*

Fig. 10 shows a type 10 diagram illustrating the influence of cyclic stress on corrosion of nitrided steel. The diagram represents results of tests to complete failure in the first or corrosion stage, and therefore represents 100 per cent damage. As only a few specimens were available, the diagram shows only approximate relationship between cycle frequency and rate of net damage.

The results indicate that the graphs, within the range of frequency investigated, are practically horizontal. In this respect, the graphs for nitrided steel resemble the graphs for other steels. Comparison of the stresses and positions of the graphs for nitrided steel with the stresses and positions of the graphs for stainless iron in Fig. 9 shows that the nitrided steel (in resistance to fatigue corrosion under these corrosion conditions) is superior to stainless iron. Nitrided steel, in resistance to fatigue corrosion in carbonate or salt water, has been found superior to any other alloy investigated.

#### *Influence of Cycle Frequency on Corrosion of Muntz Metal*

Fig. 10 shows an incomplete type 10 diagram obtained with Muntz metal. This diagram represents results of tests to complete failure in the first or corrosion stage. The experimental points and interpretative graphs, therefore, represent 100 per cent damage, instead of 15 per cent net damage as in the usual type 10 diagram.

The interpretative graphs represent stresses far above the endurance limit of Muntz metal. This probably accounts for the absence of upward curvature as the graphs extend toward the high-frequency end. As the graphs extend into the low-frequency part of the diagram, they probably curve gradually downward. The slope evidently does not become steep, however, at frequencies greater than about 1 cycle per minute. In this respect, Muntz metal probably resembles stainless iron rather than aluminum bronze. The fact that Muntz metal is subject to rapid "season cracking" indicates that under some corrosion conditions the type 10 graphs for this alloy would turn downward at abscissas representing very short corrosion time.

#### *Influence of Cyclic Stress on Corrosion of a Heat-treated Copper-nickel-silicon Alloy*

The endurance of copper and of some of the copper-rich alloys, under fatigue test at relatively high cycle frequency, is increased by contact with water. Stress-cycle graphs illustrating this fact were presented in previous papers.<sup>4,5</sup> The cooling effect of the water, rather than its corrosive effect, was evidently the predominant influence. Specimens failed by fatigue before sufficient time had elapsed for any effect of corrosion to appear.

It seemed possible, however, that if the corrosion stress, or the time before fatigue failure, or both, could be increased, effects of corrosion would be manifest. These conditions could be obtained (with a copper-rich alloy) only by using an alloy having greatest possible strength and endurance limit, and by subjecting it to fatigue corrosion at low cycle frequency. For this purpose, a heat-treated copper-nickel-silicon alloy

was selected for investigation. It was found, however, that the endurance limit of this alloy was only 25,000 lb. per square inch, about one-fourth the tensile strength. Nevertheless, this alloy was used in an attempt to obtain a type 10 diagram.

Fig. 10 shows an incomplete diagram obtained with this alloy. Points *A* and *B* represent fatigue failures at stress of 80,000 in air and in carbonate water, respectively. The horizontal lines drawn through points *A* and *B*, therefore, represent the probable times required for fatigue failure of specimens tested at various frequencies. Point *C* represents 15 per cent net damage caused by stress of 80,000 at 5 cycles per hour. At this low frequency, sufficient time has evidently been available for considerable effects of corrosion to appear.

The type 10 graph, representing corrosion-stress of 80,000, evidently extends upward from point *C* and crosses the corresponding fatigue lines drawn through *A* and *B*. Above these lines, this imaginary graph would curve as indicated qualitatively by the broken line *D*. The part of the graph below the line *B*, however, is the only part that can be investigated.

For every corrosion stress (above the endurance limit) there would be a corresponding, nearly horizontal fatigue line, above which the type 10 graph could not be investigated. By using low cycle frequencies, however, a series of the nearly vertical, low-frequency ends of type 10 graphs could be obtained. In spite of the low fatigue resistance and high corrosion resistance of this alloy, therefore, a portion of the low-frequency end of the type 10 diagram could thus be determined.

#### PART IV.—INFLUENCE OF VARYING CORROSION CONDITIONS ON THE TYPE 10 DIAGRAM

##### *Influence of Ionic Concentration on the Type 10 Diagram for Steels*

The form of the type 10 graph depends not only on the metal but also on the corrosion conditions. Results of preliminary experiments to investigate the influence of varying corrosion conditions on the form and position of the type 10 graphs are shown in Figs. 11, 12 and 13. Figs. 11 and 12 show type 10 diagrams obtained with the same steel in contact with carbonate water and with Severn River water, respectively.

Comparison of these two diagrams shows, as might be expected, that each graph in Fig. 11 is higher in the diagram than the corresponding graph in Fig. 12. The difference in position increases greatly as the graphs extend into the high-frequency end of the diagram. Abrupt upward curvature of the graphs, as they extend to the left, begins at higher frequencies for the salt-water graphs than for the fresh-water graphs. Tentative suggestion was made in a previous paper<sup>12</sup> that the upward curvature of type 10 graphs, as they extend to the left, may be

due to a limitation in the rate of diffusion of ions through the film and corrosion products. According to this idea, the nearly vertical direction of a graph at high cycle frequency would indicate that, at this frequency, the rate of diffusion of the ions (or of the dissolved oxygen) has reached a limit, which cannot be increased (under the indicated stress) by further increase in cycle frequency. If these tentative ideas are correct, the limiting rate of diffusion is evidently higher for specimens in salt water than for specimens in fresh water, and the higher limiting rate for specimens in salt water is due to the higher concentration of ions in the salt water.

#### *Influence of Water Composition on the Type 10 Diagram for Nickel*

In the type 10 diagram for nickel, shown in Fig. 7, are two graphs obtained by use of Severn River water. In spite of the scatter of results, the evidence indicates that the graphs obtained with carbonate water are higher in the diagram than the graphs obtained with salt water. Moreover, the difference in position increases as the graphs extend into the high-frequency end of the diagram. The salt-water graphs for nickel, like the salt-water graphs for chromium-nickel steel, begin their abrupt upward curvature at higher frequencies than do the fresh-water graphs.

#### *Effect of Reduced Oxygen Concentration on the Type 10 Diagram*

Fig. 13 shows a type 10 diagram obtained by fatigue-corrosion of specimens covered with cotton, as described in Part II. The experimental points and graphs in Fig. 13 represent complete failure in the corrosion stage. The damage represented by this diagram, therefore, is 100 per cent. At 10,000 r.p.m. it was found impossible to obtain satisfactory results, because the centrifugal force was great enough to prevent free penetration of water (through the cotton) to the surface of the specimen.

The type 10 graphs, within the range of frequencies investigated, are nearly horizontal. These graphs, therefore, resemble in form the graphs obtained with uncovered steel specimens. Reduction in the concentration of oxygen, in the water that reached the surface of the steel, has had practically no effect on the form of the type 10 graphs.

Each graph, however, is higher in the diagram than the corresponding graph in diagrams for uncovered steel specimens.<sup>11-13</sup> Part of this difference in position is due to the fact that the former diagram represents 100 per cent and the latter diagrams represent 15 per cent net damage. Making allowance for this, however, it can be shown that reduction in the rate of oxygen supply has raised the position of each graph in the type 10 diagram. As might be expected, therefore, reduction in the rate of oxygen supply has decreased the rate of net damage.



*Effect of Coating Specimens with Red Lead*

Fig. 13 shows a type 10 diagram obtained with steel specimens coated with red lead. The experimental points and graphs in this diagram represent complete failure in the corrosion stage. The diagram, therefore, represents 100 per cent damage. As the results of the experiments show much scatter, more experiments would be necessary to establish the exact form of the type 10 diagram. Nevertheless, graphs have been drawn to represent the most probable forms and interrelationship for the series.

Upward curvature of the graphs, as they extend to the left, begins at frequencies less than 50 r.p.m., whereas upward curvature of graphs for uncoated steel specimens begins at much higher frequencies. In this respect, the graphs for coated steel specimens resemble the graphs for aluminum alloys presented in previous papers.<sup>11-13</sup> The red lead coating, therefore, has lowered the frequency at which increase of frequency begins to lose its effect.

This change in form of the type 10 graphs may possibly be due to decrease in the rate of supply of ions to the surface of the metal. The red lead coating would also decrease the rate of supply of oxygen from the water to the metal. Whether this decrease in rate of oxygen supply would be compensated by supply of oxygen from the red lead is not known. It seems possible, however, that the effect of the red-lead coating on the form and position of the type 10 diagram is due largely to decrease in the rate of supply of ions to the surface of the metal. The coating evidently has the same qualitative effect as a decrease in the concentration of ions in the water.

The graphs for specimens coated with red lead may possibly curve downward if extended further to the right. If so, the graphs would resemble qualitatively the graphs for monel metal presented in previous papers.<sup>12,13</sup>

The diagram for specimens coated with red lead furnishes additional evidence that the form of a type 10 diagram depends not only on the metal, but also on the corrosion conditions. The form of a type 10 diagram is evidently influenced greatly by the properties of the coating whether the coating be corrosion products or other material.

**PART V.—INFLUENCE OF STRESS RANGE ON CORROSION***General Description of the Type 11a Diagram*

Type 11a diagrams illustrate the relationship between corrosion stress and the time necessary to cause constant net damage, or the relationship between corrosion stress and the rate of net damage. Abscissas, according to the direction in which they are measured, represent either corrosion times or rates of net damage.

Type 11a diagrams, corresponding to most of the type 10 diagrams discussed in Parts III and IV, are assembled in Fig. 14. The time scale is indicated at the bottom and the rate scale is indicated at the top of the figure. The rate scale applies only to diagrams representing 15 per cent net damage, and hence does not apply to the lowest diagram in Fig. 14. Logarithmic scales are used for both coordinates. Time abscissas are measured from right to left. This arrangement is to facilitate study of each type 11a diagram together with the corresponding type 10 diagram, as two views of a three-dimensional diagram. The type 11a diagrams in Fig. 14, however, will be discussed as two-dimensional diagrams.

#### *Type 11a Diagrams for Ordinary Steels*

As shown in previous papers,<sup>9-13</sup> type 11a graphs for ordinary steels (on a logarithmic scale) are nearly straight and nearly parallel. There is some evidence, however, that the slope decreases slightly with decrease in cycle frequency.

Two diagrams in Fig. 14 represent the steel BW-W-10, which is represented by type 10 diagrams in Figs. 11 and 12. The graphs in these two type 11a diagrams are practically straight and not far from parallel. The slope possibly decreases slightly, however, with decrease in cycle frequency. The graphs representing corrosion in carbonate water, as might be expected, are higher in the diagram than the corresponding graphs representing corrosion in salt water. The difference in position is greater for the high-frequency graphs than for the low-frequency graphs.

#### *Type 11a Diagram for Cotton-covered Steel Specimens*

The lowest diagram in Fig. 14 represents results obtained with cotton-covered specimens. This diagram should be compared with the type 10 diagram for cotton-covered specimens shown in Fig. 13. Both diagrams represent 100 per cent. damage.

The type 11a graphs for cotton-covered specimens are evidently nearly straight and nearly parallel. These graphs are higher in the diagram than are the corresponding graphs for steel BW-W-10, which represent corrosion in water with free access of air. Moreover, the slope of the graphs is less for the cotton-covered specimens than for specimens with free access of air. These differences are not due entirely to the fact that the former graphs represent greater net damage than do the latter graphs.

#### *Type 11a Diagrams for Nickel, Aluminum Bronze, Monel Metal and Duralumin*

Type 11a diagrams for nickel and for aluminum bronze are shown in Fig. 14. In general form, the two diagrams are similar. They both

resemble, also, the type 11a diagrams for monel metal and duralumin, presented in previous papers.<sup>12,13</sup>

In regions representing low stresses, all the graphs of each series are nearly straight and nearly parallel. As they ascend, the graphs representing low cycle frequencies (50 per minute or less) remain nearly straight and nearly parallel. The graphs representing higher cycle frequencies, however, curve to the right. The higher the frequency, the more abrupt is the curvature. The abruptness increases also with decrease in the thermal conductivity. The evidence seems to indicate that the curvature of the high-frequency graphs is due largely to thermal influences.

### *Type 11a Diagram for Stainless Iron*

A type 11a diagram for stainless iron is shown in Fig. 14. This diagram corresponds to the type 10 diagram in Fig. 9.

In spite of the wide scatter of individual results, the type 11a graph representing 1450 r.p.m. is fairly well established. The evidence indicates that this graph, below an ordinate representing about 40,000 stress, is nearly straight. Above about 40,000 stress, the graph curves abruptly to the right. The abrupt curvature of this high-frequency graph is probably due to thermal influences. Because of the low thermal conductivity of stainless iron, thermal influences are more prominent in this alloy than in ordinary steels.

The other graphs in the type 11a diagram for stainless iron have been drawn parallel to the nearly straight portion of the 1450 r.p.m. graph. This arrangement of the diagram is based on collateral evidence presented in the other diagrams of Fig. 14.

### *Equation Representing Influence of Stress on Corrosion*

The evidence seems to indicate that, for all metals, the relationship between corrosion-stress and the rate of net damage is approximately a logarithmic straight-line relationship. Thermal effects, especially at high cycle frequencies and high stresses, may introduce other variables and thus mask the straight-line relationship. At low cycle frequencies, the straight-line relationship extends over a wide range of corrosion stresses.

The logarithmic straight-line relationship between corrosion-stress and rate of net damage means that the rate of net damage varies as a power of the corrosion stress. The relationship between corrosion stress and rate of net damage may be represented by the equation

$$R = CS^n$$

in this equation,  $R$  represents the rate of net damage, and  $S$  represents the corrosion-stress. The exponent  $n$  is numerically equal to the cotan-

gent of the angle of slope of the type 11a graph.  $C$  is a constant depending on the corrodibility of the metal, on the corrosiveness of the environment and on the cycle frequency.

According to this equation, the rate of net damage depends on two factors, a corrosion (and frequency) factor  $C$  and a stress factor  $S^n$ .

#### *Power Exponent for Various Metals*

The slope of the low-frequency graphs of the type 11a diagram for any metal may be used in obtaining the value of  $n$ . As shown in Fig. 14, the slopes of the low-frequency graphs differ greatly for different metals. The cotangents of the angles of slopes for the diagrams in Fig. 14, and for similar type 11a diagrams in previous papers,<sup>12,13</sup> have been estimated, and the approximate results are given in Table 4.

TABLE 4.—*Values of  $n$  for Various Alloys under Indicated Corrosion Conditions*

Alloy	Corrosion Conditions		Net-damage, Per Cent.	$n$
	Water	Oxygen Supply		
Ordinary steels.....	Carbonate	Normal	15	3.0 to 4.0
Ordinary steels.....	Salt	Normal	15	3.0 to 4.0
Ordinary steels.....	Carbonate	Reduced	100	5.0
Stainless iron.....	Carbonate	Normal	15	4.7
Monel metal.....	Carbonate	Normal	15	2.6
Nickel.....	Carbonate	Normal	15	5.7
Aluminum bronze.....	Carbonate	Normal	15	4.5
Aluminum alloys.....	Carbonate	Normal	15	3.0

It should be emphasized that the values for  $n$  in Table 4 apply only to the indicated corrosion conditions. With one exception, these values of  $n$  represent results obtained with water having free access to air.

The high value for  $n$  obtained with the cotton-covered steel probably is not due entirely to the fact that the net damage was 100 per cent. The high values of  $n$  for the cotton-covered steel and for stainless iron are probably due to the correspondingly low values of  $C$ . Evidence, to be presented in a later paper, indicates that (for steels at least) decrease in the corrosion factor  $C$  is accompanied by increase in  $n$ .

#### *Influence of Steady Stress on Corrosion*

The relative influence of steady stress and cyclic stress on the rate of net damage, as explained in Part III, is illustrated by the form of type 10 graphs, such as the graphs for aluminum bronze in Fig. 8. The nearly vertical portions at the low-frequency ends of these graphs, therefore,

may be assumed to represent the influence of equivalent steady stresses. The rates of net damage due to these equivalent steady stresses are represented by the corresponding abscissas of the points of intersection of the graphs with the lower boundary *B*.

Using these abscissas, and using the indicated half ranges of cyclic stress as ordinates, corresponding points have been plotted in the type 11a diagram for aluminum bronze in Fig. 14. Through these points the line *B* has been drawn. (Line *B*, though plotted in a type 11a diagram, is not a type 11a graph. In the list of types, given in a previous paper,<sup>10</sup> this type was called type 12). As the ordinates of this diagram do not represent equivalent steady stresses, the absolute position of line *B* does not represent the influence of steady stress on corrosion. In its slope and in its position with reference to the other graphs of the diagram, however, this line represents approximately the influence of steady stress.

As indicated by line *B*, the relationship between steady stress and the rate of net damage is probably a logarithmic straight-line relationship. The slope of this line indicates that the rate of net damage, for aluminum bronze, varies as at least the fifth power of the steady tensile stress.

### *Intercrystalline Corrosion of Metals under Stress*

Intercrystalline failure of metals under stress, as in season cracking of brass and in the so-called "caustic embrittlement" of boiler steel, is probably due to corrosion pitting, differing chiefly in its location from ordinary sharp, deep corrosion pitting.

The general conditions that favor intercrystalline corrosion pitting are: (1) relatively high stress, (2) low cycle frequency, (3) slight intensity of corrosion, (4) very little accumulation of corrosion products. These conditions cause sharp, deep corrosion pitting, whether or not the pitting is chiefly in the grain boundaries.

Under such conditions, stressless corrosion would be slight. Net damage, therefore, is a large proportion of total damage. In other words, *C* is small and *S\** is relatively great. As implied in the discussion of Table 4, decrease in the corrosion factor *C* (for any metal) is probably accompanied by increase in *n*. Under the general conditions favoring intercrystalline corrosion, therefore, the rate of net damage increases enormously with increase in stress.

Intercrystalline attack has been attributed by some investigators to specific chemical action. Peculiar powers of intercrystalline attack have been attributed to specific reagents. It seems probable, however, that too much emphasis has been laid on the assumed specific character of intercrystalline attack. The reagents that have been considered specific probably are the reagents that furnish in high degree the general conditions described for intercrystalline corrosion.

Such general conditions are represented by the nearly vertical, low-frequency portions of some type 10 graphs, such as the high-stress graphs for aluminum bronze in Fig. 8. Microscopic examination of specimens represented by these portions of type 10 graphs has not yet been made. It is improbable, however, that in all such graphs the low-frequency portions represent intercrystalline corrosion. However that may be, graphs actually representing intercrystalline corrosion would undoubtedly be similar in form to the nearly vertical, low-frequency portions of the type 10 graphs for aluminum bronze.

### *Application to Design of Machinery and Structures*

Application of the results of the investigation of fatigue-corrosion to the design, construction and operation of machinery and structures can be discussed only in a general way. It should be evident that a single numerical value, such as a "corrosion-fatigue limit," cannot be used as a complete index or criterion of a process influenced by the many variables that operate in fatigue corrosion. The problem requires intelligent application of the principles involved in the equation  $R = CS^n$ , with due consideration for the influence of cycle frequency as represented by type 10 diagrams. As the order of merit of a series of metals may vary considerably with variation in the cycle frequency, comparison of metals on the basis of data obtained at some one cycle frequency may be misleading. Use of both types of two-dimensional diagram, therefore, is necessary in studying this subject. The subject is best studied by means of three-dimensional diagrams.

### SUMMARY

Special attention is given to nickel, aluminum bronze, stainless iron, nitrided steel and Muntz metal. Each experiment was in two stages: (1) a corrosion stage, in which the specimen was corroded with or without cyclic stress; (2) a fatigue stage, in which the specimen was tested to fatigue failure and the fatigue limit was estimated. The lowering of the fatigue limit is used as a measure of the "damage" due to corrosion.

Diagrams of three types are presented: Type 5 illustrating relative influence of stressless corrosion and corrosion under cyclic stresses, in causing damage; type 10 illustrating influence of cycle frequency on net damage, and type 11a illustrating influence of stress range. These diagrams, in addition to diagrams for steels, aluminum alloys and monel metal presented in previous papers, illustrate the behavior of a great variety of metals under similar conditions of corrosion.

Preliminary data are given to illustrate influence of varying corrosion conditions on the forms of the net-damage diagrams. Influence of varying water composition and oxygen content, and influence of red-lead coating, are discussed.

The type 10 (frequency) diagram is probably of the same qualitative form for all metals and corrosion conditions, but the quantitative form and position vary. The form and position are influenced greatly by the properties of the coating whether of corrosion products or other material. The type 10 diagram also illustrates the relative influence of cyclic stress and steady stress.

The rate of net damage varies as the third to at least the fifth power of the corrosion stress, depending on the metal, cycle frequency and corrosion conditions.

The general conditions favoring intercrystalline corrosion are discussed. Application of stress-corrosion data to design, construction and operation of machinery and structures is discussed briefly.

#### ACKNOWLEDGMENTS

Acknowledgment is due to the following personnel of the Naval Engineering Experiment Station: To Captain H. R. Greenlee, U. S. N., Officer in Charge; Lieutenant Commander Weber, Lieutenant Haven and Lieutenant Ward, for interest and cooperation. To Mr. W. C. Stewart, associate metallurgist, who acted as engineer of tests, for very valuable assistance in carrying on the experiments. To Messrs. A. P. Vandermast, laboratorian, L. E. Foster, foreman, and J. K. Amoss, quartermen machinist, for assistance in the investigation. Acknowledgment is also due to the International Nickel Co., the Aluminum Co. of America, the Ludlum Steel Co., the American Brass Co., and Mr. W. M. Corse for generous cooperation by supplying material.

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### NOTE TO FIGURES

In the diagrams, the phrase "at this point" means that the fatigue limit, estimated from a two-stage experiment, is as indicated in the diagram. The phrases "above this point" and "beyond this point" mean that for some reason the position in the diagram could not be estimated definitely from this experiment, but is estimated to be above or beyond the position indicated.

The arrow tips used in some of the diagrams indicate by their direction either that a specimen failed in the first stage of a two-stage experiment, or that, in order to reduce the resultant fatigue limit to the chosen value, the corrosion time must be greater than the value indicated by the position of the arrow tip.

In Fig. 14, the indicated "rates of net damage" do not apply to the diagram for AU-O-10.

### DISCUSSION

(*E. M. Wise presiding*)

B. P. HAIGH, Greenwich, England (written discussion).—Dr. McAdam's investigations are of equal interest to practical engineers and to theorists. From the practical standpoint, it would be unfortunate if the dangers of "corrosion-fatigue" were overestimated. In England, the first recognition of the action was coupled immediately with efforts to overcome the trouble, and these efforts have been in some degree successful. The steel-wire ropes used for towing Paravanes under sea water vibrated with high frequencies in curves that corresponded to bending the rope over an imaginary pulley of diameter about 500 times that of the rope; and the moderate range of stress induced by this vibration resulted in rapid fracture under sea water. The trouble has been greatly delayed and, for the practical purposes in view, almost completely eliminated by protecting the wires with a thin layer of zinc applied by "hot galvanizing" or by "Bruntonising."<sup>16</sup> Dr. McAdam's work on red lead as a protective coating is therefore of special interest.

Dr. McAdam's comparative tests on different steels explain an experience that

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<sup>16</sup> B. P. Haigh: Chemical Action in Relation to Fatigue in Metals. *Inst. Chem. Engrs.* (March, 1929).



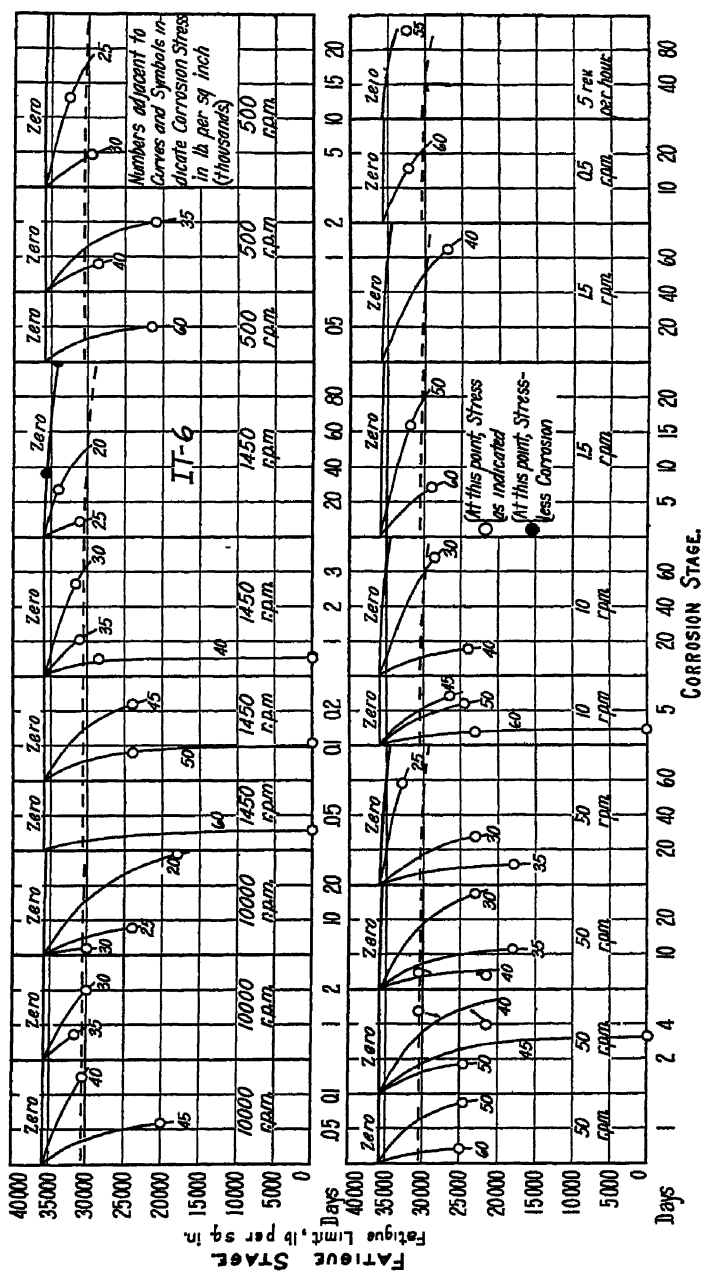


FIG. 1.—TYPE 5 DIAGRAMS, NICKEL, IT-6.

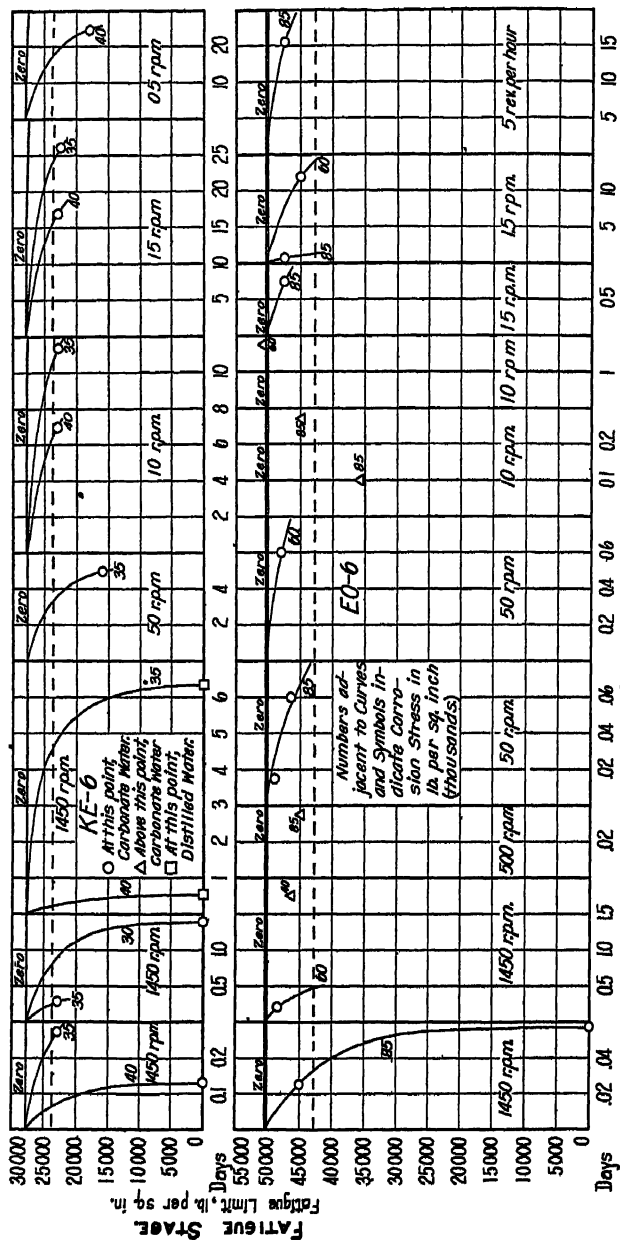


FIG. 2.—TYPE 5 DIAGRAMS, NICKEL AND ALUMINUM BRONZE.

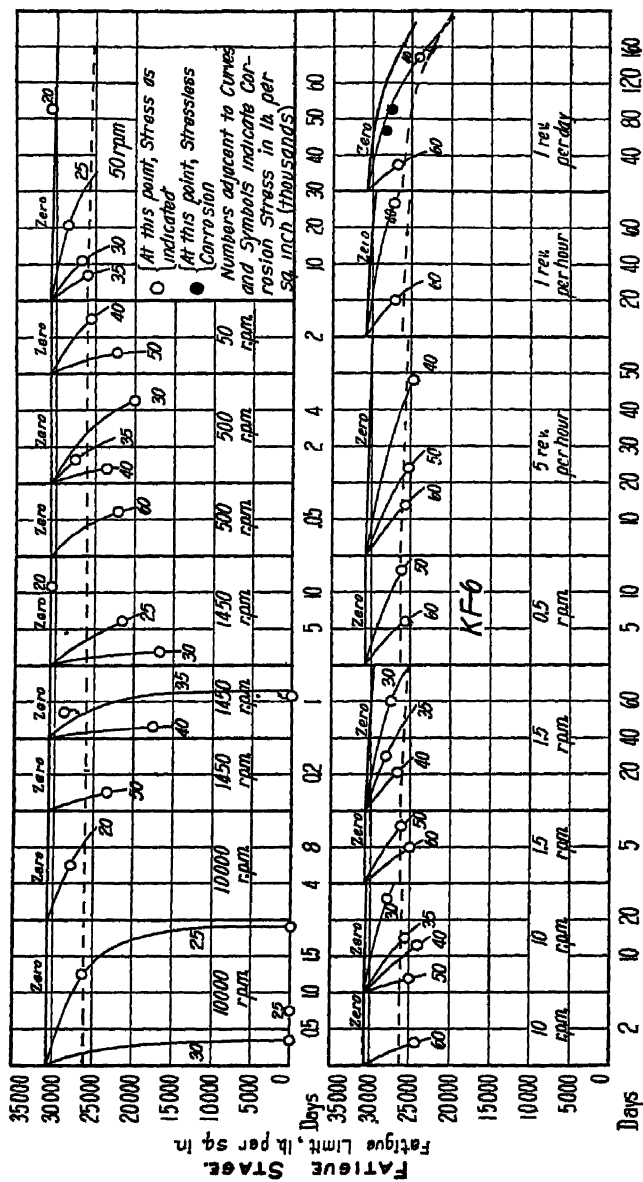


Fig. 3.—Type 5 Diagrams, ALUMINUM BRONZE, KF-6.

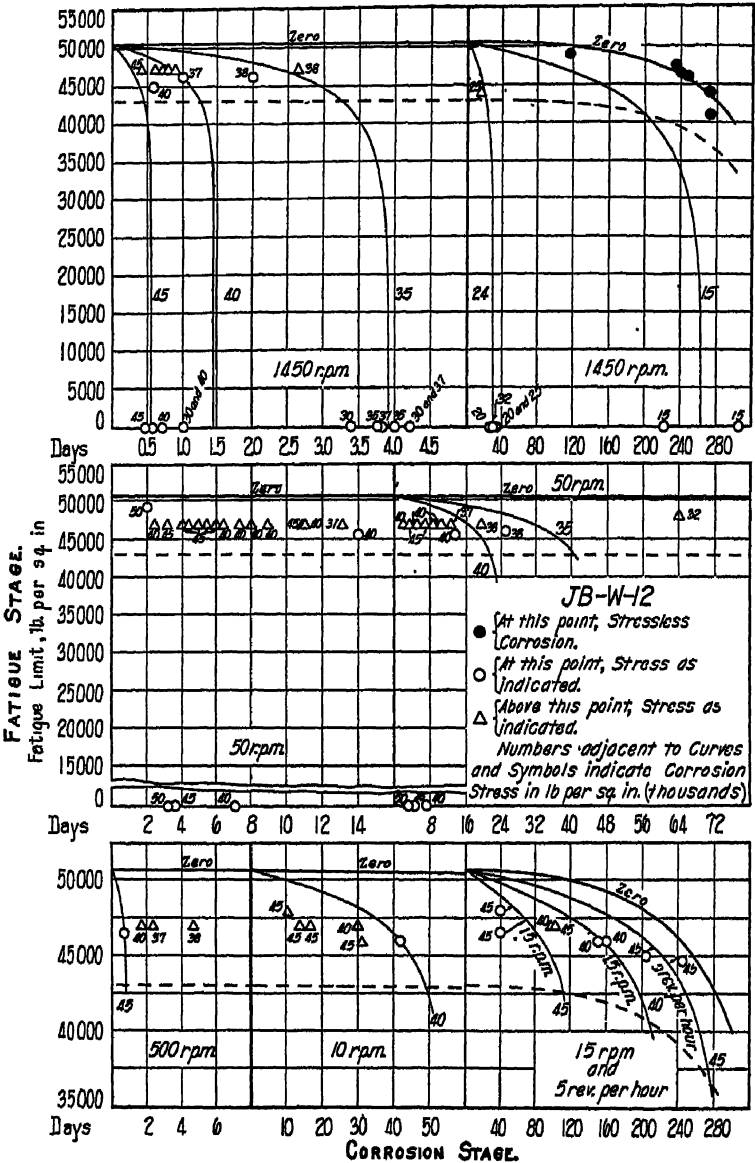


FIG. 4.—TYPE 5 DIAGRAMS, STAINLESS IRON.

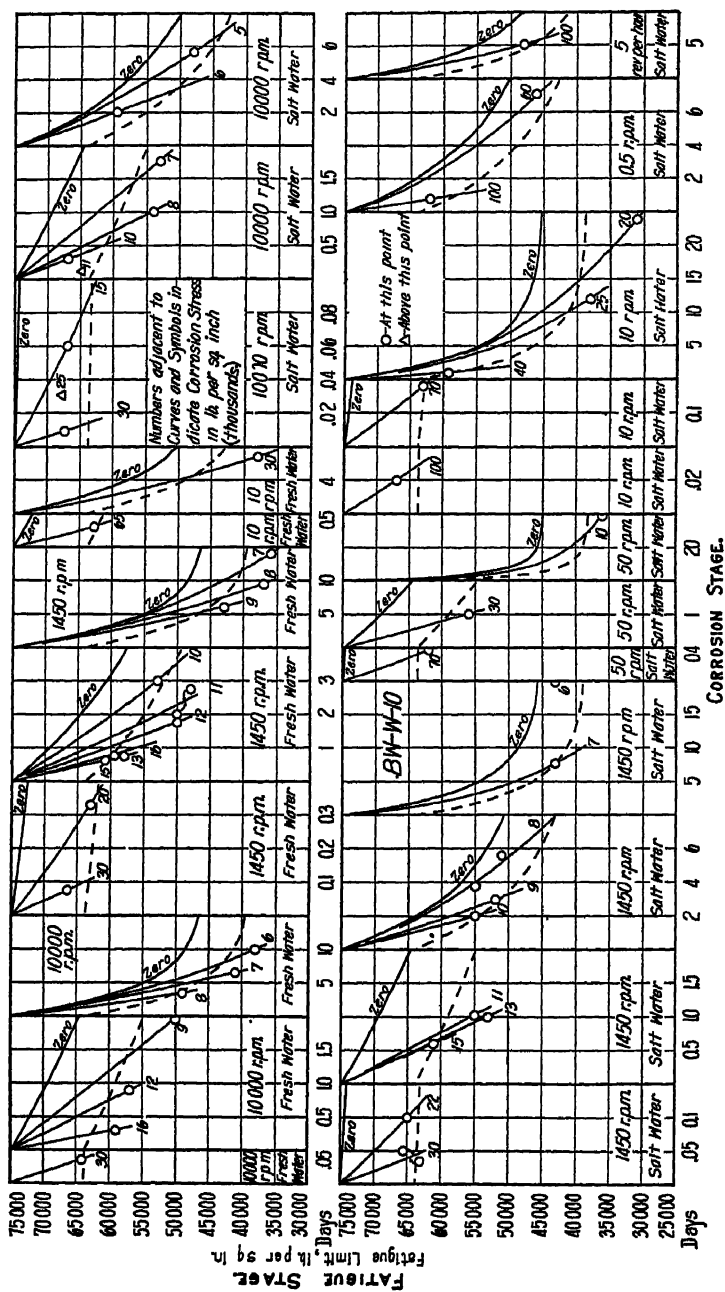


FIG. 5.—TYPE 5 DIAGRAMS, CHROMIUM-NICKEL STEEL.

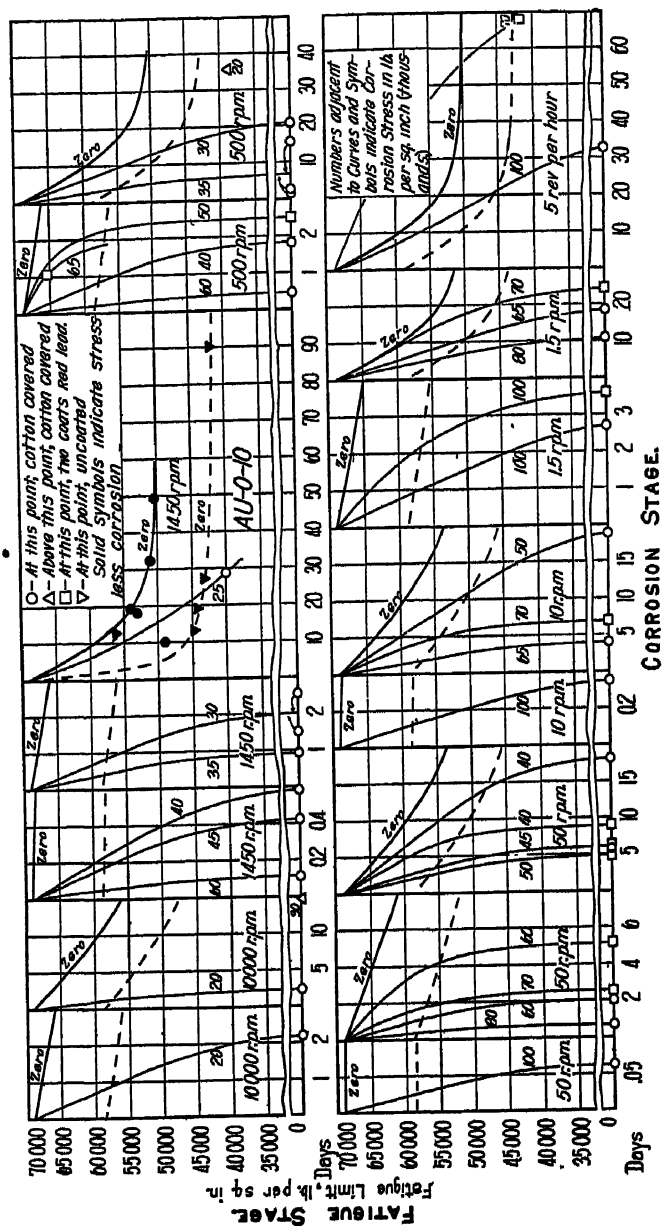


FIG. 6.—TYPE 5 DIAGRAMS, CHROMIUM-NICKEL STEEL, COVERED WITH COTTON AND WITH RED LEAD.

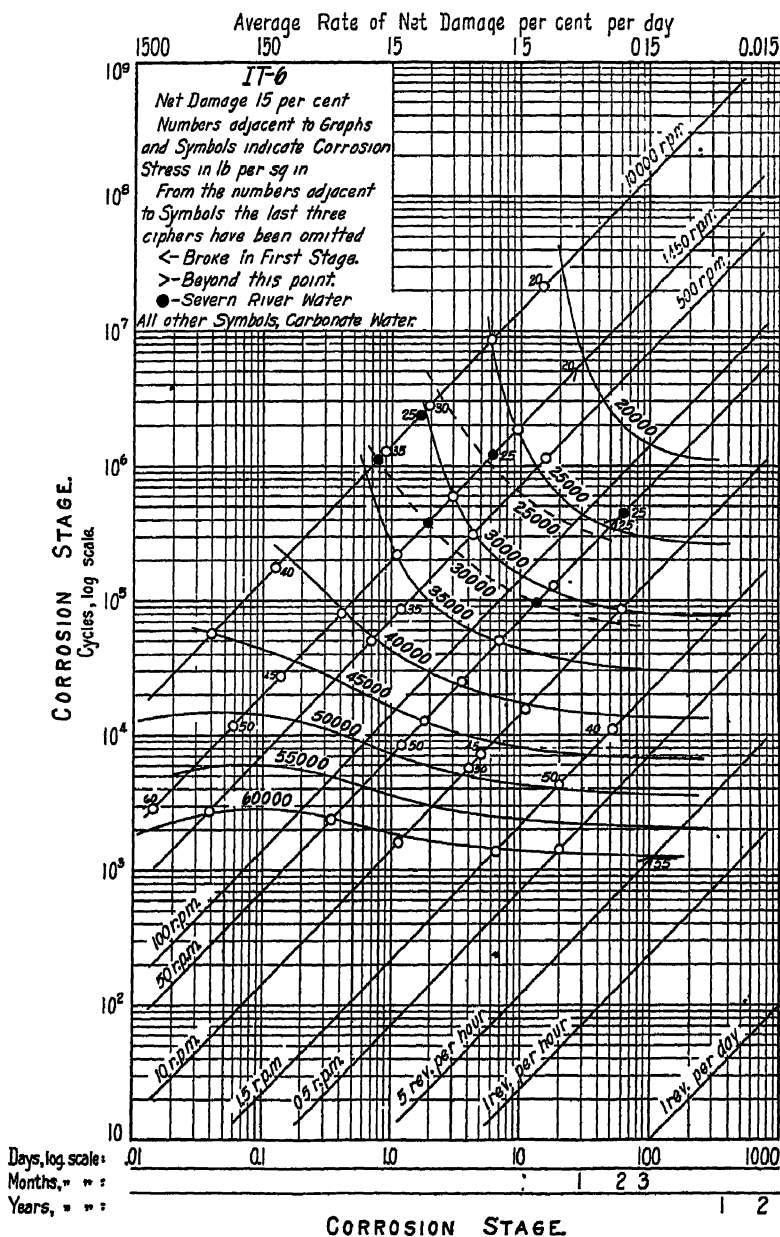


FIG. 7.—TYPE 10 DIAGRAM, NICKEL, IT-6.

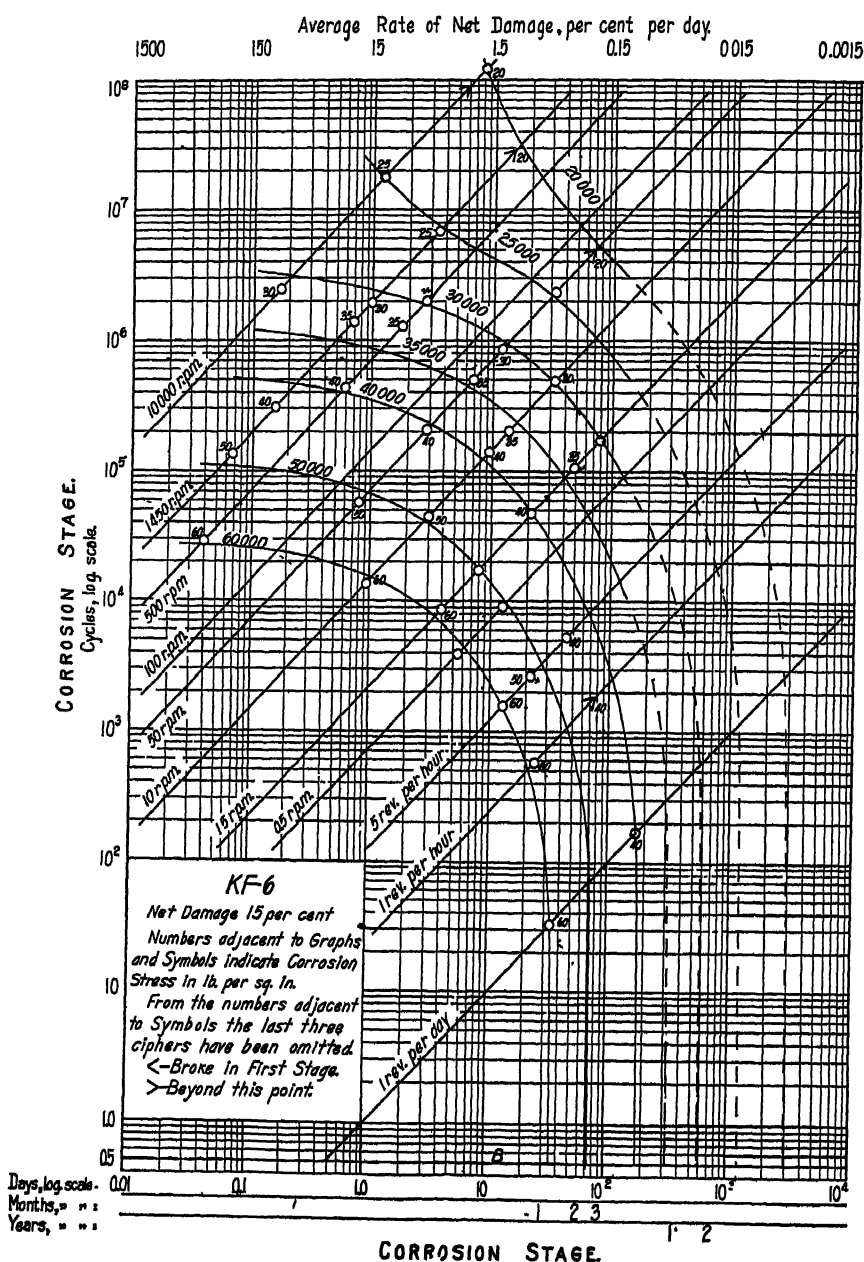


FIG. 8.—TYPE 10 DIAGRAM, ALUMINUM BRONZE.



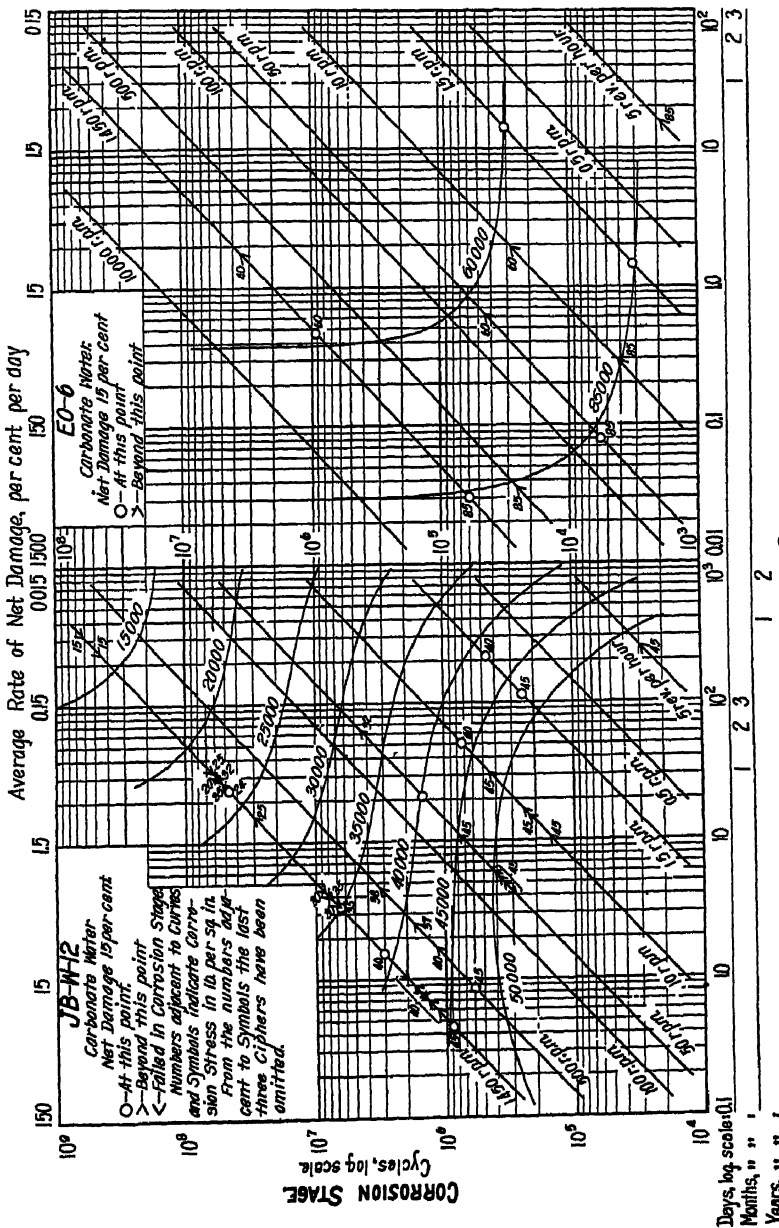


FIG. 9.—TYPE 10 DIAGRAMS, STAINLESS IRON, JB-W-12 AND NICKEL EO-6.

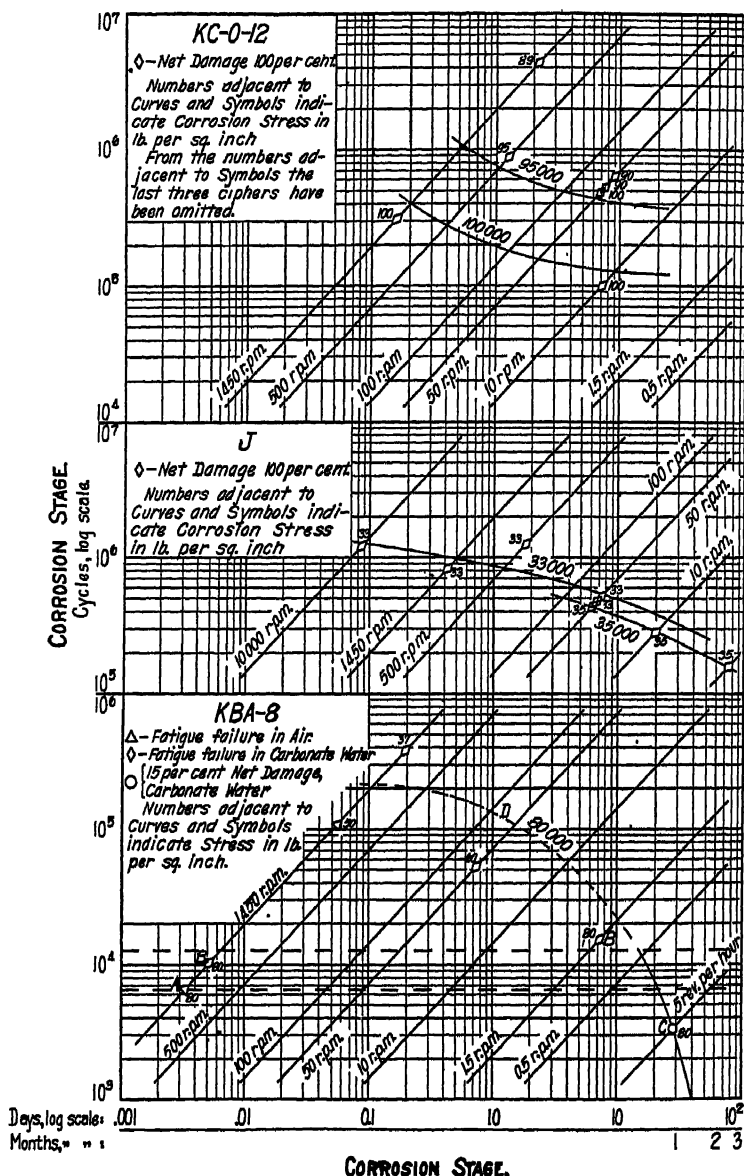


FIG. 10—TYPE 10 DIAGRAMS, NITRIDED STEEL, KC-O-12, BRASS, J AND HEAT-TREATED COPPER ALLOY, KBA-8.

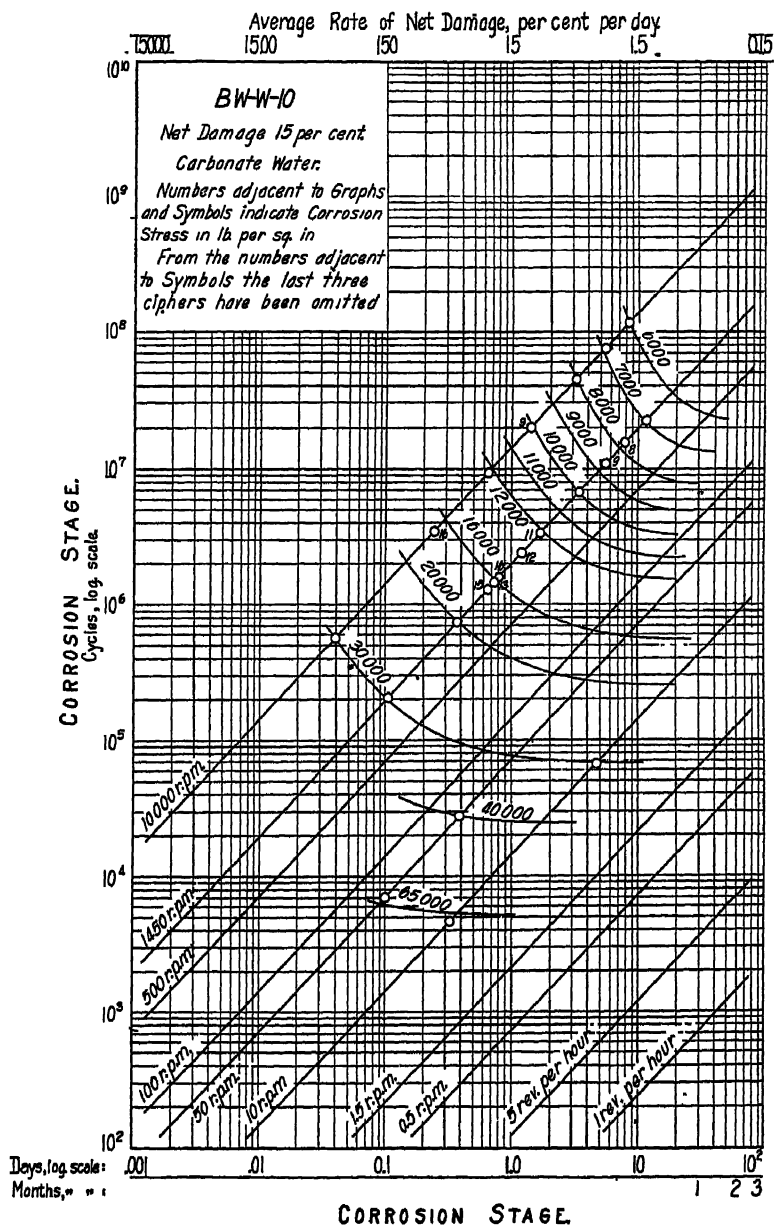


FIG. 11.—TYPE 10 DIAGRAM, CHROMIUM-NICKEL STEEL, CARBONATE WATER



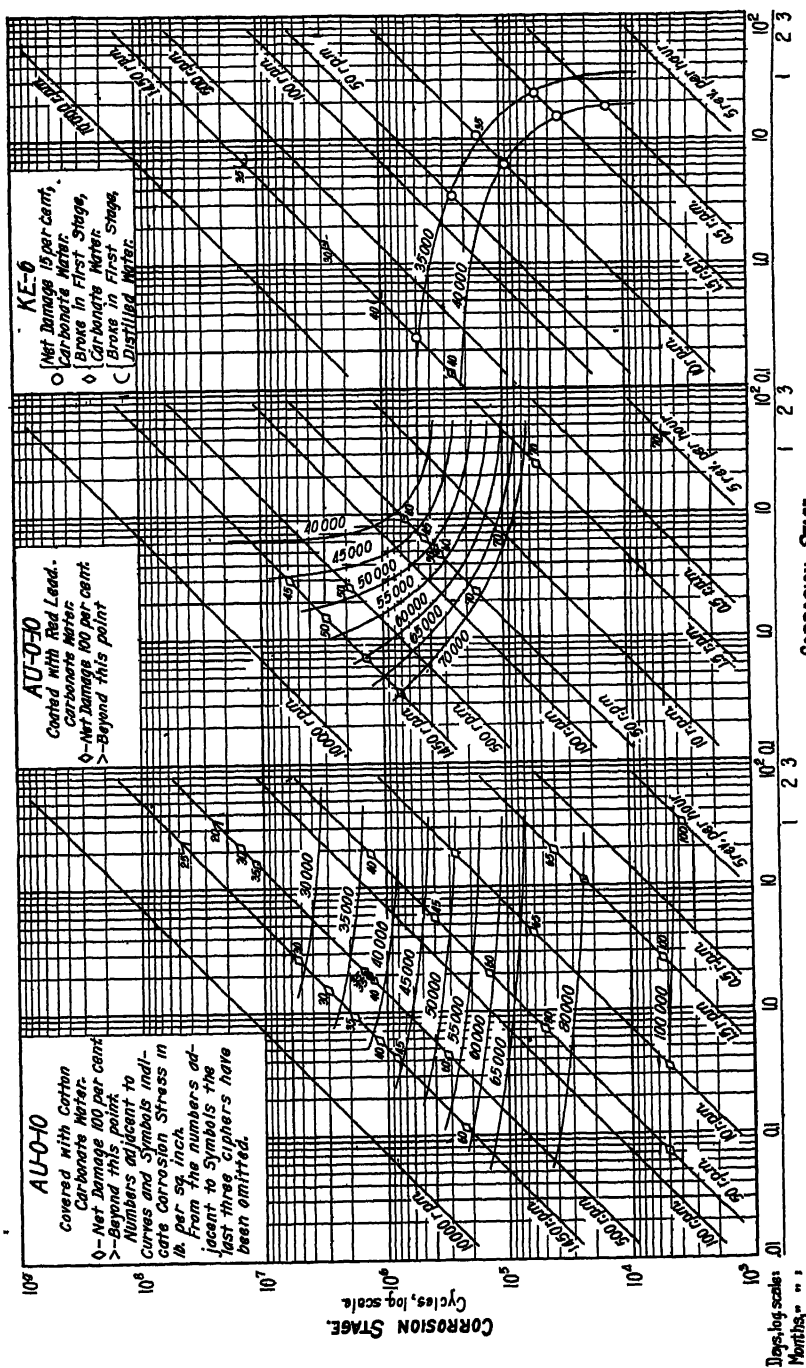


FIG. 13.—TYPE 10 DIAGRAMS, CHROMIUM-NICKEL STEEL, AU-O-10 AND ALUMINUM BRONZE, KE-6.

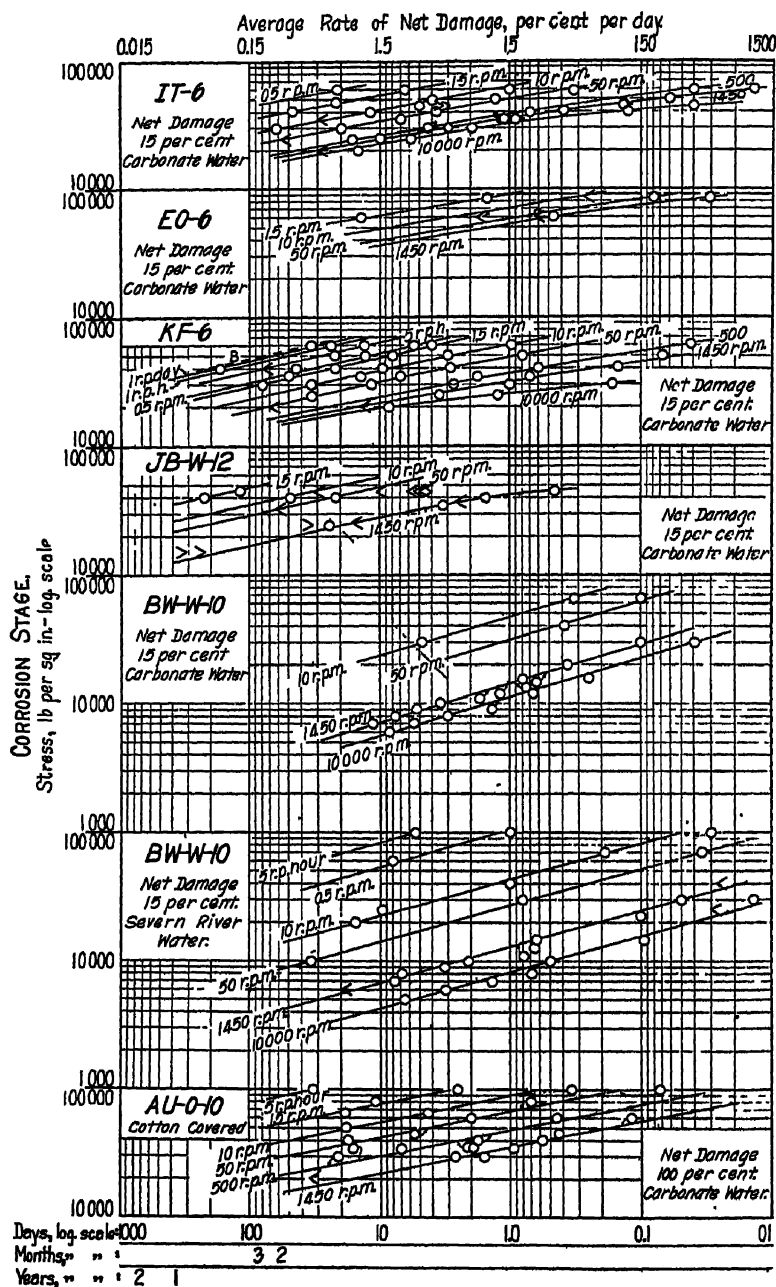


FIG. 14.—TYPE 11c DIAGRAMS, VARIOUS ALLOYS.

at first puzzled the Paravane engineers. In their earlier tests, and so long as the wire was not protected from the water, steels of different qualities with different tensile strengths gave nearly equal and very poor results under water; but when the wires were protected, the endurance obtained in practice were not only improved but widely different for different qualities of steel: Dr. McAdam's investigations show that corrosion-fatigue is seldom important in mild steels, and that few high-tensile steels are superior to ordinary mild steel when exposed to conjoint chemical and mechanical action provoking fatigue.

Whereas Dr. McAdam tested a wide variety of different metals and alloys with an extremely restricted choice of chemical reagent—focusing attention on the actions of fresh and salt water—investigators in England have studied fewer materials but used a greater variety of chemical reagents. Comparison of the results led to the conclusion that water—the commonest of all reagents encountered in practice—was probably the most active of all. The view expressed by Dr. McAdam, that oxygen ions are probably the active agents of chemical action in most of the examples studied, is now supported by a great deal of independent research and appears worthy of special attention as a base from which further investigation may attack and possibly overcome the difficulty. When Jenkin and Lehmann in 1925 endeavored to verify the phenomena of corrosion-fatigue, and obtained only negative results with boiling solutions of strong reagents, it was suggested that these boiling solutions lacked the oxygen necessary for the action. The suggestion, at the time, may have appeared to many to be nothing more than the despairing hope of an embarrassed experimenter; but in 1929, Jenkin and Binnie<sup>17</sup> found themselves able to report that a corrosion-fatigue limit of 7.5 tons per sq. in., observed with a cold solution of salt sprayed through air, was raised to 11.8 tons per sq. in. when the same solution was sprayed on the same steel through an atmosphere of hydrogen; and they expressed also the opinion that the limit might be raised further—towards the normal air fatigue limit at 18.3 tons per sq. in.—by eliminating “every trace of oxygen.”

In 1917, the present writer pointed out that steel pieces broken by fatigue in air occasionally showed signs of oxidation on the faces of the fracture; and there seems good reason to believe that atmospheric oxygen as well as oxygen in solution occasionally plays the part of a chemical reagent, provoking fatigue. In 1930, Haigh and Jones<sup>18</sup> described an investigation in which special efforts were made to eliminate oxygen in fatigue tests on lead and lead alloys; and it was shown that an oil bath or even a thick layer of grease delayed fatigue, although it might not necessarily raise the fatigue limit. It was shown further that a bath of acetic acid successfully eliminated fatigue in lead and the lead alloys used, under all the ranges of stress that could be applied without causing excessive plastic yield. The latter conclusion appears all the more remarkable in view of the active corrosion that occurred during the tests—which were prompted by the anticipation that nascent hydrogen—liberated from the acid attacking the surface of the metal—might combine with any oxygen present, leaving none free to enter the metal and provoke fatigue.

The number of independent variables that have to be considered in investigating conjoint chemical and mechanical actions is so great that the resources of graphic representation are severely strained in presenting the conclusions reached; but the special diagrams introduced by Dr. McAdam are now becoming more familiar, and have proved serviceable. The continuity of the graphs throughout the field of investi-

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<sup>17</sup> A. M. Binnie: *The Influence of Oxygen on Corrosion Fatigue*. Reports and Memoranda No. 1244, Aer. Res. Comm. (1929).

<sup>18</sup> B. P. Haigh and B. Jones: *Atmospheric Action in Relation to Fatigue in Lead*. Inst. Metals (1930).

gation supports the view that the injury to the surface is caused by one and the same chemical action in the different circumstances; but I do not think it negatives the view that fatigue fracture may be due to a conjoint chemical and mechanical action different from that causing the injury to the surface. The experiment on lead described above indicates that fatigue may be eliminated although surface injury is exceedingly violent; and I think it is important to maintain the view advanced many years ago that the two kinds of injury may in certain circumstances at least arise from distinctly different actions—both of which can be regarded as conjoint chemical and mechanical actions.

T. M. JASPER, Milwaukee, Wis. (written discussion).—There is no question but that the strength of a steel specimen or part is reduced by corrosion, and that the stress imposed by a definite load is progressively increased by corrosion attack. There is no question but that the searching effect of fatigue in combination with corrosion on such parts will show this up much more clearly than will static testing.

Some of Dr. McAdam's results indicate that under corrosion-fatigue certain specimens will fail eventually at so low a stress that one might say that the corrosion endurance limit is practically zero. The time at which these specimens show failure at nearly zero stress is so short in days, representing a relatively few million cycles of stress, that one is led to ask the question: Does this represent what one may expect under service conditions, or does the test as conducted represent an overemphasized effect of corrosion-fatigue? I shall not attempt to answer this question authoritatively because of my limited knowledge and experience on the subject, but I am sincerely of the opinion that overemphasis has been placed on the effect of corrosion-fatigue by the general conditions of testing assumed by Dr. McAdam, because the results presented are not corroborated in the technical press as they would be if service conditions produced very frequent failures at exceptionally low stresses.

There is no question but that Dr. McAdam has done an admirable piece of work in focusing attention on corrosion-fatigue. It has been suggested to me that ways and means should be employed to reduce this effect by protecting, if possible, the part under fatigue from corrosion attack. I should very much like to ask the author to undertake the task of informing designing engineers as to how his work should be practically and quantitatively applied in designing and operating service equipment. This is asking a great deal, because service conditions are so variable; nevertheless the application of a phenomenon is of great importance to builders and users of equipment.

Some light has been thrown on this matter by Mr. Fuller in his paper on the endurance properties of some well known steels in steam.<sup>19</sup>

T. S. FULLER, Schenectady, N. Y.—This paper constitutes another very valuable contribution by Dr. McAdam to the subject of corrosion fatigue, in which he has attempted to express quantitatively what many of us have observed qualitatively.

In our studies of the corrosion-fatigue of 3.5 per cent nickel steel in steam atmospheres, we have found substantially these values. The endurance limit of the nickel steel in air at room temperature is 58,000 lb. per sq. in. When the specimens on which the endurance limit was determined were exposed to an atmosphere of wet steam and air for one week without stress and then tested in air at room temperature, the endurance limit became 50,000 lb. per sq. in. However, when tests were made on specimens previously uncorroded with a jet of wet steam blowing on the specimen in the atmosphere—in other words, a condition of stress plus corrosion—the endurance limit

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<sup>19</sup> T. S. Fuller: Endurance Properties of Steel in Steam. *Trans. A. I. M. E., Iron and Steel Div.* (1930) 280.



of the same material became 24,000 lb per sq. in. The difference between the 50,000 and the 24,000 is due to the presence of the stress, and the values corroborate those reported by Dr. McAdam. If the specimens were first corroded for one week in the atmosphere of wet steam and air and subsequently tested with the jet of wet steam blowing on the specimens in the atmosphere, the endurance limit became 14,000 lb. per square inch.

E. M. WISE, Bayonne, N. J.—Apparently one of the worst elements is oxygen. Unfortunately, we have to breathe it, but aside from that the remarks of Dr. Haigh are particularly interesting. His results might indicate that if a metal is corroded actively enough the damaged surface may be removed as fast as it is formed, and the material actually will be stronger in respect to fatigue than material that is not being actively corroded. I do not subscribe to his views that this effect is due solely to the absence of oxygen on the surface of the material. That could be readily tested by corroding material actively by making it anode, and I am inclined to think that if the conditions were such that the sample did pit but corroded smoothly the corrosion-fatigue values would be very high, perhaps higher than normal air-fatigue values.

Probably the most important fact brought out in this paper is that nitrided steel showed exceptionally high values for corrosion-fatigue. Unfortunately, the particular method employed for nitriding these samples is not given and there is no means of knowing whether it is normal nitrided surface or exceptionally heavy hardened surface.

Mr. Fuller's experiments on nitrided steel indicate that it is extremely good under corrosion-fatigue, which is in agreement with the present findings.

D. J. McADAM, JR. (written discussion).—With much of Professor Haigh's discussion I am in agreement. My comment will be confined to points in which I do not agree with his views.

Professor Haigh's statement that "corrosion-fatigue is seldom important in mild steels" may tend to give incorrect impressions. As the composite graphs in my later paper<sup>20</sup> show, the influence of stress on net damage due to stress corrosion, for all carbon and ordinary alloys steels in carbonate water, is practically the same. The influence of stress on corrosion-pitting depends on the applied stress, not on the strength of the metal. As oxygen is one of the most important factors in ordinary corrosion, it would evidently be one of the most important factors in stress corrosion. With Professor Haigh's emphasis on the importance of oxygen, I am in agreement. His comments in regard to "two kinds" of "conjoint chemical and mechanical action," however, give no clear picture of his ideas. The student of corrosion is continually impressed with the great variety of its manifestations. It is not surprising, therefore, to find an equal variety in the manifestations of stress corrosion. The variety is even greater because of the introduction of two additional variables, stress and cycle frequency. The idea that corrosion-fatigue may be due to a mysterious chemical action that is not corrosion, therefore, seems unnecessary and unsubstantiated.

The behavior of lead, described by Professor Haigh cannot be discussed readily in detail by one who has not made stress-corrosion experiments with this metal. Nothing is apparent in the results as described, however, that cannot be explained by consideration of known data on stressless corrosion, stress corrosion and the influence of notches. As shown in my later paper, net damage, and probably total damage, may be greater under slight than under severe general corrosion. The observed damage as measured by lowering of the fatigue limit depends on the depth and sharpness of pit-

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<sup>20</sup> D. J. McAdam, Jr.: Influence of Water Composition on Stress Corrosion. *Proc. Amer. Soc. Test. Mat.* (1930) **31**, II, 259.

ting and on the stress concentration due to the pitting. Stress concentration in a soft metal such as lead would be very slight even under severe pitting. Furthermore, because of its low recrystallization temperature, lead at room temperature shows some of the characteristics shown by most metals at elevated temperatures. It is possible, therefore, that lead (under stress corrosion) is pitted more selectively and deeper by atmospheric corrosive attack than by the more severe general attack of an aqueous solution. For most metals at room temperature the reverse is true.

Professor Jasper's idea that my investigation of stress corrosion has been confined to severe corrosion conditions is incorrect. That his idea is incorrect should be evident from a consideration of the great variety of metals and alloys that have been tested in contact with water. The intensity of corrosive attack of the water on these metals covered a very wide range. With some metals, corrosion was negligible, with others it was severe. Comparison of the effects of water on ordinary steels and on stainless steels, for example, is practically a comparison of the effects of severe and slight corrosive attack on the same metal. The two classes of steel in their behavior toward corrosive agents differ chiefly in the protective efficiency of the surface films, not in the susceptibility of the underlying metal.

To one familiar with corrosion conditions as in service, however, Professor Jasper's idea that severe corrosion conditions are practically never encountered in actual service is somewhat surprising. As examples, I mention only the use of metals in the oil fields and in steam boilers. Even if severe corrosion could be as readily avoided as Professor Jasper seems to think, however, it would be well to know the effects of accidental contact of metals with severe corrosive attack. As an example, I mention the fact that large shafts of marine vessels, when they come in contact with water through inefficiency of protective devices, very frequently fail under very low stresses. Since the reasons for these formerly mysterious failures are now understood, greater effort is being made to prevent contact of water with marine shafting.

Corrosion, even severe corrosion, is still an important problem. It seems probable that this problem and the closely related problem, the influence of stress on corrosion, will continue of importance for some time.

# Machinability of Free-cutting Brass Rod

BY ALAN MORRIS,\* BRIDGEPORT, CONN.

(New York Meeting, February, 1932)

BRASS rod for use in automatic screw machines is one of the major products of the brass mills. A large tonnage is consumed each year in the manufacture of an endless variety of finished articles and parts for assembly into other products. The machines that do this work have been developed to a high degree of efficiency, and their manufacturers are still striving for higher production speeds. This development has brought with it a demand for brass rod to meet the increasingly difficult machining conditions.

This paper is a report of the results of tests undertaken in an effort to obtain a measure of the effects of such variables as lead content, microstructure and cold work on the machinability of brass rod.

It is realized that the term "machinability" has never been well defined. Power, finish and tool life all should have a place in such a definition. In practice it is sometimes found necessary to sacrifice some of these in order to obtain a rod that will not tend to throw up a burr, or will give a burr which is easily tumbled off. Again a specially stiff rod may be necessary because of long overhang from the chuck or a rod of special characteristics is needed to take a given broaching operation without chattering. It is only through an understanding of the effect of basic mill operations on the machinability of the rod that such problems as these may be solved most economically. It is hoped that this paper, together with the discussion it may evoke, will prove to be a basis for such an understanding.

## TESTING APPARATUS

The testing apparatus used was of the single-tooth milling cutter type, in all respects similar to that first used and described by Airey and Oxford<sup>1</sup> and again by Boston.<sup>2</sup> The machine used in the present test is shown in Fig. 1.

It is an ordinary milling machine in which a heavy pendulum has been substituted for the pulley on the arbor. If the pendulum is raised

\* Research Engineer, Bridgeport Brass Co.

<sup>1</sup> J. Airey and C. J. Oxford: On the Art of Milling. *Trans. Amer. Soc. Mech. Engrs.* (1921) 43, 549.

<sup>2</sup> O. W. Boston: Test Methods for Determining the Machinability of Metals. *Trans. Amer. Soc. Steel Treat.* (1929) 16, 659.

to any given height and allowed to fall freely, it will rise almost to the same height at the opposite end of its swing. A pointer is carried around by the pendulum and remains at this point to indicate on a dial the angle through which the pendulum has risen. If the sample is brought into position so that the tool, as it is carried around with the pendulum, will make the desired cut, and the weight is allowed to fall from the same height as before, it will rise to a lesser height due to the resistance of the sample to the cutting tool. The difference between these two heights, multiplied by the mass of the swinging pendulum, is a measure of the

energy consumed in making the cut. It is assumed that the energy lost by elastic distortion of the machine is negligible, or at least sufficiently constant so that the results on different samples are comparable.

The pendulum, including the weight and the arm, weighed  $49\frac{1}{4}$  lb. The center of gravity of the swinging system traveled on an arc of radius  $23\frac{3}{4}$  in. The tool was of the cut-off type,  $\frac{1}{8}$  in. wide, and except where otherwise stated had neither front rake nor side rake. Its cutting edge traveled on an arc of radius  $1\frac{3}{4}$  inches.

#### TESTING METHOD

While the apparatus is similar to that used previously by other investigators, the method differs radically. In the present tests the sample was first carefully weighed.

It was then clamped firmly in the machine. With the pendulum hanging vertically, the sample was brought up until the cutting edge of the tool just touched its upper surface. The pendulum was retracted and latched in its raised position. The sample was then elevated 0.020 in., so that when the pendulum was released the tool would remove a chip from the surface of the sample having a maximum thickness at the center of approximately 0.020 in., and thinning down to zero at either end. The angular reading corresponding to the highest position reached by the pendulum on its upward swing was recorded. The pendulum was then swung freely from the same starting position and the angular reading again taken. The sample was moved over so that the next cut would be taken at a fresh spot. This was repeated till

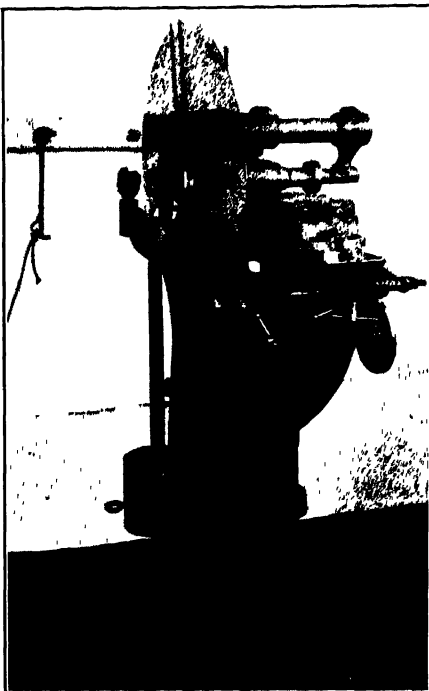


FIG. 1.—TESTING APPARATUS.

six cuts had been made. The sample was again carefully weighed, the difference between the original and final weight being taken as the weight of metal removed. The volume of metal removed was calculated from its known specific gravity and weight removed as determined experimentally. The total energy consumed in making the six cuts, as calculated from the angular readings, divided by the volume of metal removed, gives us directly the energy consumed in removing a unit volume of metal. All cuts were made without lubrication.

The results of the present tests are expressed in foot-pounds per cubic inch of metal removed. In this paper, the results so expressed will be spoken of as "unit cutting energy." They must be considered as purely comparative, because the numerical results vary considerably when, for instance, a series of tests is made on the same specimen with varying depth of cut. Fig. 2 is a plot of the results of such a series.

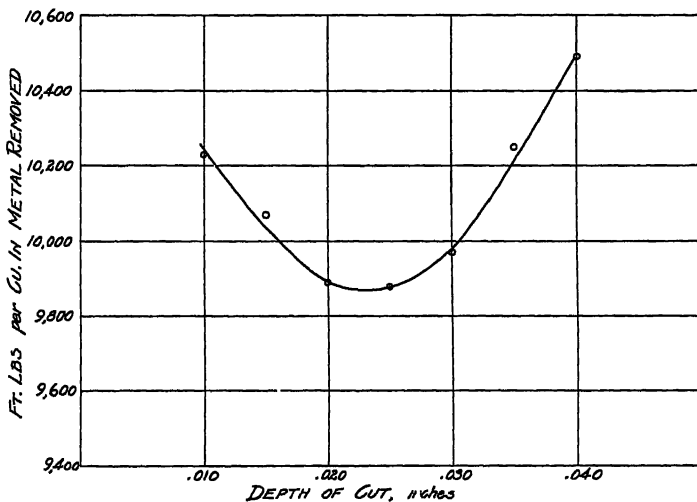


FIG. 2.—VARIATION OF RESULTS OF TESTS WITH DEPTH OF CUT.

Change in tool shape is also reflected in the numerical results. Table 1 gives the results of tests made on various materials, both with the standard rakeless tool and with a tool having a 25° front rake.

Front rake on a tool reduces the unit cutting energy considerably. In practice, variations of tool shape, speeds and feed, lubrication and other factors render it impossible in the present state of our knowledge to base a prediction of power consumption on tests of this nature.

Tests made under identical conditions, however, are useful in making comparisons between samples of materials which do not differ too widely in their characteristics.

Free-cutting brass rod is usually extruded at a size somewhat larger than the desired finished size. The extrusion is followed by annealing

TABLE 1.—*Tests with Rakeless Tool and Tool with 25° Rake*

Material	Composition, Per Cent					Other Elements, Per Cent	ft-lb. per Cu In Metal Removed	
	Cu	Sn	Pb	Fe	Si		No Rake	25° Rake
Monel metal	30 0			1 45	0 023	Ni, 67 90	40,400	25,700
Silicon-tin bronze	Rem	1 77		0 008	1 00	Mn, 1 00	24,500	15,520
Silicon-manganese bronze	96 21			2 99		Mn, 0 80	23,500	17,970
Tin bronze	Rem.	1.36		0 008	0 044		23,030	14,260
Phosphorus copper	Rem.			0 005		P, 0 014	22,570	16,900
Tough-pitch copper	Rem					O, 0.10	17,730	12,450
Free-cutting brass rod	60 95		3 16	0 07		Zn, rem	10,490	8,795

and cold-drawing operations. The most obvious variables, therefore, to be studied in their relation to machinability of the finished rod are (1) alloy, (2) microstructure, (3) amount of cold drawing.

#### EFFECT OF VARIATION IN ALLOY

Within the range of copper contents met with in practice, the unit cutting energy seems to depend largely on the percentage of lead present. A series of samples containing varying percentages of lead were secured and annealed for 1 hr. at 500° C. Table 2 gives their analyses. In Fig. 3 are plotted the results of the tests.

TABLE 2.—*Analyses of Samples Used in Tests to Show Effect of Variation in Lead Content on Unit Cutting Energy*

Composition, Per Cent				ft-lb. per Cu In Metal Removed
Cu	Sn	Pb	Fe	
60.70	none	0.02	0.01	24,700
59.95	none	0.33	0 026	14,200
60.41	none	0.62	0.010	13,350
63.40	none	1.47	0.03	11,690
63 00	none	1.82	0.03	11,200
63 25	none	2.04	0 01	10,800
63.43	none	2 55	0.03	10,440
61.61	0.08	3.13	0.06	10,160
60.76	none	3.13	0 03	10,100
61.08	0 05	3.18	0.05	10,080
60 54	none	3 33	0.03	10,000
60 82	none	3 37	0 03	9,890
61.13	0.08	3 43	0.06	9,760

The copper contents of this series vary from 60.0 to 63.5 per cent, yet when the test results are plotted against lead content, the points form a smooth curve. Within this range, then, it would seem that lead

content is the dominant factor in determining machinability. Variation in copper probably does exert a small influence, but in this series of samples it seems to have been masked effectively by the effect of lead variation. A test on unleaded brass containing 66.6 per cent of copper gave a unit cutting energy of 27,400 ft.-lb. per cubic inch of metal removed. An unleaded Muntz metal containing 60.7 per cent copper gave a result of 24,700 ft.-lb. per cubic inch of metal removed.

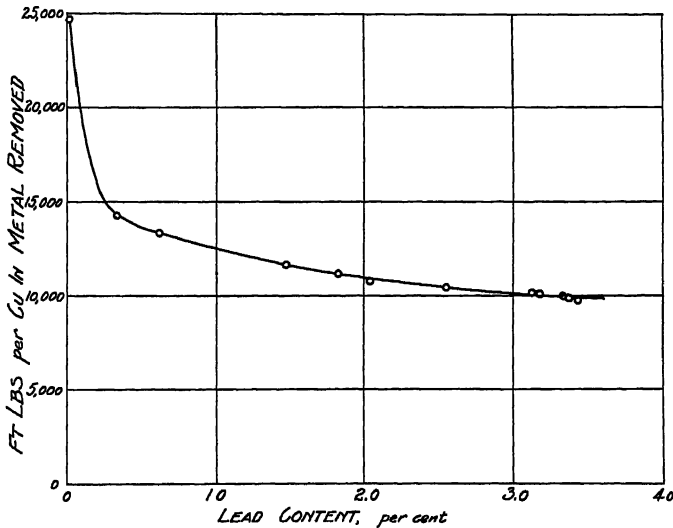


FIG. 3.—RESULTS OF TESTS ON SAMPLES LISTED IN TABLE 2.

The curve in Fig. 3 indicates that a small amount of lead added to a Muntz metal will produce a decided improvement in its machinability. It also shows that comparatively little is to be gained by increasing the lead content above 3.0 per cent. It will be shown later that the effects of microstructure and cold drawing are much greater than that of a change of lead content from 3.0 to 3.5 per cent.

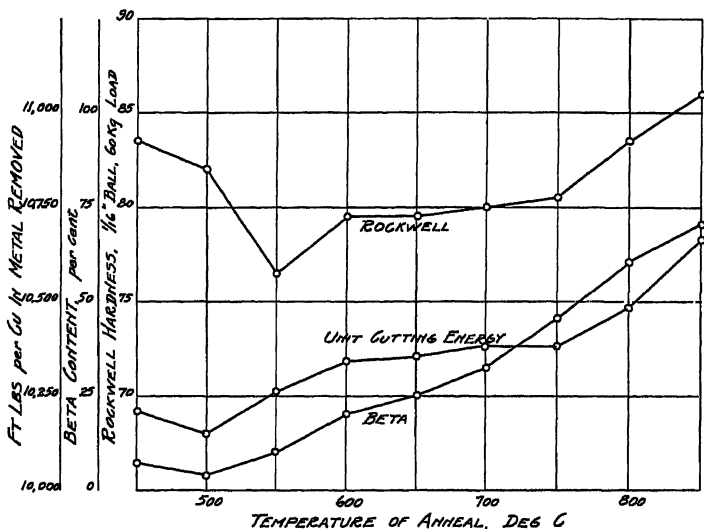
No tests have as yet been made to determine the effect of the usual impurities, such as tin and iron.

#### EFFECT OF MICROSTRUCTURE

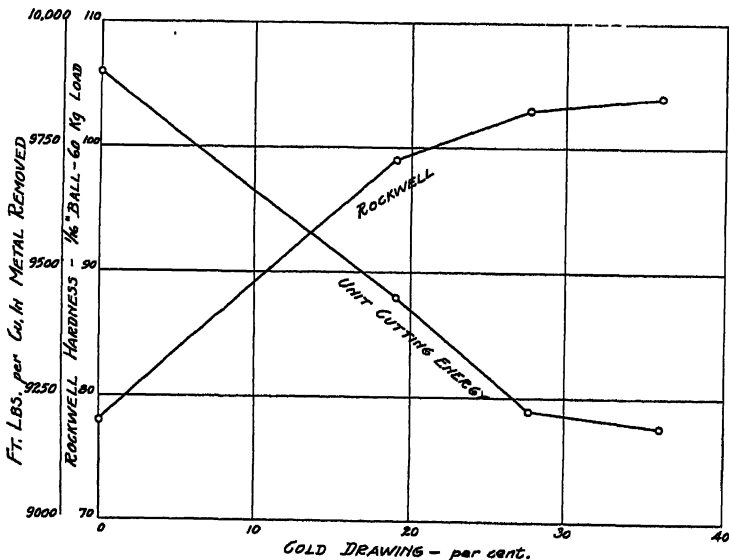
A series of samples, all cut from the same bar, were annealed at various temperatures for 2 hr. and quenched. They had the following composition: Cu, 59.6 per cent; Sn, 0.09; Pb, 3.4; Fe, 0.1; Zn, rem. Each sample was examined microscopically and an attempt was made to estimate the percentage of beta present. The Rockwell hardness of each was also determined, using a  $\frac{1}{16}$ -in. ball with a 60-kg. load. The results are plotted in Fig. 4.

# MACHINABILITY OF FREE-CUTTING BRASS ROD

The original hard-drawn sample contained about 10.0 per cent of . At 450° C. some beta was dissolved, but the hardness was high use of very fine grain size. At 500° C. more beta has gone into



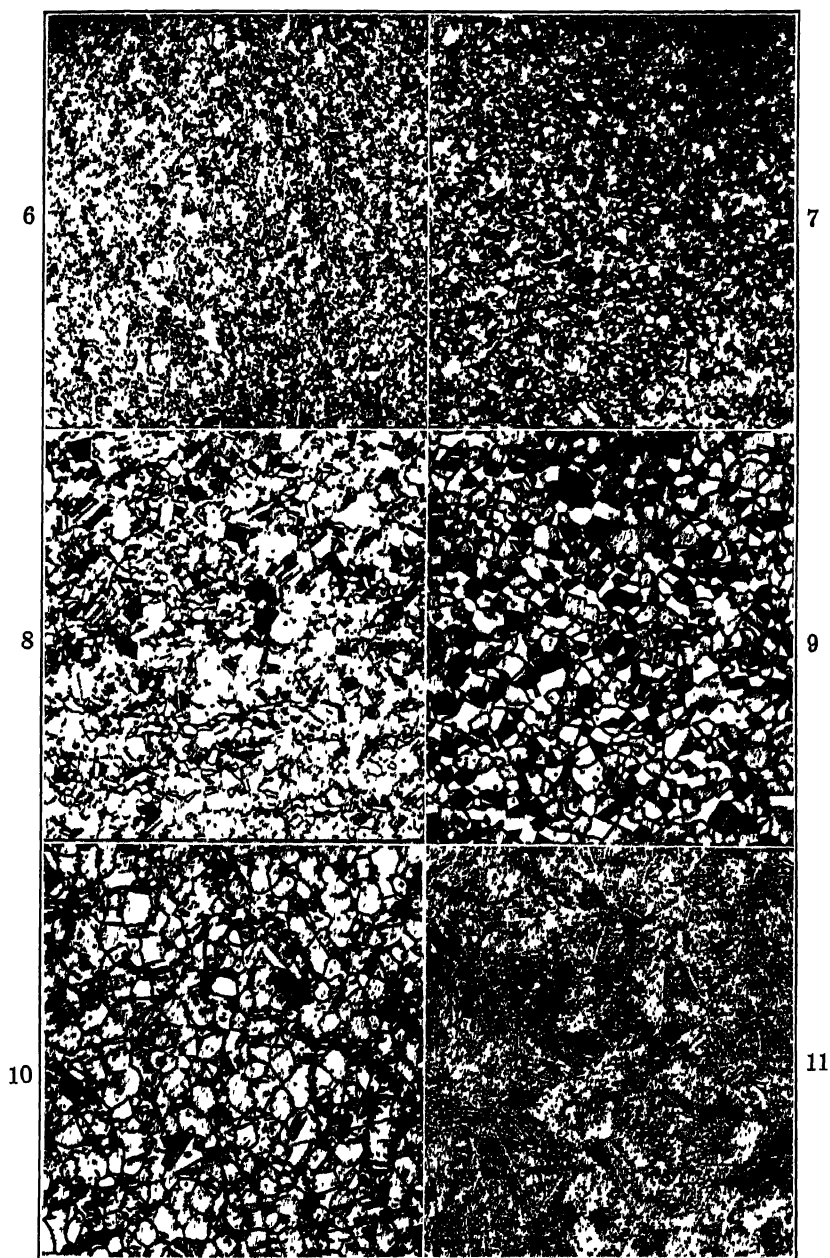
4. RELATION BETWEEN HARDNESS, BETA CONTENT AND UNIT CUTTING ENERGY OF SAMPLES ANNEALED AT VARIOUS TEMPERATURES.



5.—RELATION BETWEEN UNIT CUTTING ENERGY AND DEGREE OF COLD DRAWING.

tion, with very little increase in grain size. The hardness has dropped atly. At 550° C. the grain size has increased sufficiently to more a offset the effect on hardness of the increase in beta. Throughout





FIGS. 6-11.—LONGITUDINAL SECTIONS ( $\times 75$ ) OF SAMPLES USED IN TESTS PLOTTED IN FIG. 4, ETCHED WITH AMMONIA AND HYDROGEN PEROXIDE.

All annealed 2 hr. and quenched, temperatures of annealing being, respectively, 450° C., 500° C., 550° C., 650° C., 750° C. and 850° C.

is lower range the unit cutting energy curve follows the beta curve, and does not reflect the higher hardness values due to fine grain size. The point of maximum machinability (lowest energy consumption) corresponds with the point of minimum beta content. Photomicrographs showing longitudinal sections of some of these samples are shown in figs. 6 to 11 inclusive.

### EFFECT OF COLD DRAWING

The effect of cold drawing has been investigated a number of times, and in all cases cold drawing has been accompanied by a considerable improvement in machinability. The curve plotted in Fig. 5 is typical.

In two instances, however, the first light draw produced a small increase in energy consumption, which was followed by consistent decrease with further cold work. The sample used in the tests plotted in Fig. 5 had the following composition: Cu, 59.6 per cent; Sn, 0.09; Pb, 3.4; Fe, 0.10.

### RELATION OF TENSILE PROPERTIES TO MACHINABILITY

The tensile strength of a Muntz metal increases and its ductility decreases with rise in beta content and with cold drawing. It has been shown that machinability decreases with rising beta content and improves with cold working. It is evident therefore that the machinability of a given piece of brass rod cannot be predicted through consideration of its tensile properties. In his discussion of the paper by Boston mentioned earlier in this paper, H. L. Daasch suggested that shearing strength, as a function of elongation and shearing strength, might be used to indicate relative machinability. No work of this nature has as yet been undertaken.

### SUMMARY AND CONCLUSIONS

1. A rapid and inexpensive machinability test is described.
2. Machinability of Muntz metal improves rapidly with small additions of lead, but much less rapidly as the lead content increases. Within the range of 60.0 to 63.5 per cent, the effect of copper content is small.
3. Machinability of annealed leaded brass rod is harmfully affected by the presence of beta.
4. Machinability is improved by cold drawing after annealing.
5. Tensile properties cannot be expected to indicate machining quality of a rod.

### ACKNOWLEDGMENTS

The author's grateful acknowledgments are due Mr. W. R. Webster, whose suggestion these tests were undertaken, Mr. J. L. Christie for helpful suggestions and the Bridgeport Brass Co. for permission to publish the results.

## DISCUSSION

(John R. Freeman, Jr., presiding)

F. V. HARTMAN, New Kensington, Pa. (written discussion).—The author mentions the term "machinability" and states that power, finish and tool life all should have a place in the definition of this term. Nothing is said in regard to the type of cuttings. This would seem to be a rather important factor of machinability for many machining operations. It may not be so important a factor in connection with brass, but it is for other materials such as steel, monel metal and some aluminum alloys. For instance, a material that produces continuous and stringy cuttings is none too satisfactory for machining in many automatic screw machine operations, drilling deep holes or tapping threads.

According to the curve in Fig. 2, it would seem that the most desirable depth of cut to use would be 0.023 in., corresponding to the lowest portion of the curve, instead of 0.020 in. With this depth of cut, the probable error would be reduced appreciably in that a slight plus or minus variation in the depth of cut would make very little difference in the unit cutting energy, whereas with a 0.020-in. depth of cut a slight minus variation in the depth of cut would result in an appreciable increase in the unit cutting energy. Has the author any data to explain the shape of the curve of Fig. 2? It would seem probable that the increase in unit cutting energy for cuts less than 0.023 in. deep is caused by energy absorbed before the tool starts cutting. In other words, when making a shallow cut the cutter comes in contact with the surface of the specimen when the angle between the cutter and the surface is so near 90° that the cutter probably rides over the surface for a short distance before it begins to penetrate, causing the cutter arbor and the work-holding jig to spring apart somewhat. This would seem to act like a brake and would absorb considerable energy without removing any metal. This tendency could be determined by taking a second cut. The rise of the curve for increasing depth of cut, deeper than 0.023 in., is no doubt largely accounted for by the friction of the sides of the cutter.

Possibly the speed of cutting is partly responsible for the deep dip of the curve, Fig. 2, as it would seem that the rate at which the metal is removed might have a bearing on the unit cutting energy. Obviously, the deeper the cut, the slower would be the rate at which the tool makes its cut, and it is quite likely that the energy required to remove metal may increase as the speed decreases, as the speed of testing in a tensile test affects the results obtained. If the power instead of the energy required to remove the metal were plotted against depth of cut, possibly a much flatter curve would result. It would be interesting to know whether the author has any data to show what effect the speed of cutting has upon the energy required.

No mention is made of the average cutting speeds at which these tests were made. It would seem desirable to know these speeds and to see how they compare with the cutting speeds generally employed in the machining of brass. Obviously, the results of these tests will be more comparable with machine-shop practice if the cutting speeds are somewhat alike than if there is a wide difference.

The author concludes that "a rapid and inexpensive machinability test is described." Although he has made a very interesting determination, the term machinability is no doubt intended in a limited sense and not in the full sense of the term. While power, finish and tool life are referred to in the introduction as being factors of machinability, none of these have been determined. Neither finish nor tool life has been touched upon. The only determination has been unit cutting energy and this is only one factor of cutting power.

There is little doubt that the author's results shed considerable light on the problem of machinability of brass in milling operations, and it is probable that they also

pertain to other machining operations. It might be suggested, however, that the next logical step would seem to be to coordinate his results closely with actual shop practice.

O. W. BOSTON, Ann Arbor, Mich. (written discussion).—It seems unfortunate that some type of tests more directly associated with metal-cutting processes could not have been used. The form of cut used does not correspond with any type of test previously used in the study of machinability of metals. This would not be objectionable, if outstanding improvements were shown. To obtain energy values from several specimens, which would be comparative, all bars would have to be the same diameter. Otherwise, slight errors would be introduced. A small error in elevating the table for the depth of cut would make a great difference in the energy per chip, inasmuch as the length of the cut is maximum for the depth of cut selected. It is, of course, impossible to get the predetermined depth of cut each time, owing to the possible error in reading the knee-elevating gage, or in establishing the zero point indicating the contact between the cutter and work.

The writer has found that when the width of the cutter such as that used by Mr. Morris is below 0.200 in., the cutting force falls below the straight line, indicating the energy as a function of the width of cutter, assuming the cut to be taken on a land. While the energy values obtained with the 0.125-in. wide cutter may be comparative, they might be misleading if they were used as absolute values.

The writer does not understand the curve in Fig. 2, which shows that the foot-pounds per cubic inch of metal removed is high when the depth of cut is 0.010 in., reaches a minimum at a depth of about 0.023 in., after which it is high again and maximum when the depth is maximum at 0.040 in. One fundamental law, well established in metal cutting, is that thick chips are removed more efficiently than thin ones. This applies to all types of cutting and metals. It would appear, therefore, that in Fig. 2 the depth of cut is not the only variable which influences the energy per cubic inch of metal removed. The increase in energy per cubic inch for depths greater than 0.023 in. is due, undoubtedly, to some fault of the test. It may be that, as the chip is formed on the face of the single-tooth cutter which has zero front and back rake, the metal is pushed from the center toward the side, exerting undue friction on the wall of the groove formed. This frictional resistance would be greatest for the greatest depth. Also, the length of cut through which this friction acts is greatest for the greatest depth. It is probable, also, that the lowest point of the curve shown in Fig. 2 would be located at greater depths for wider tools.

The conclusions set forth in the paper are indeed interesting. It would, unquestionably, be desirable to correlate the machinability data as determined by the pendulum miller with tool-life tests, inasmuch as tool life is the factor in which manufacturers are most interested. Tool life is a direct function of cutting speed and, therefore, production.

Fig. 4 shows that as beta increases there is practically no difference in unit cutting energy or Rockwell hardness for annealing temperatures of 600° to 750° C., inclusive, while above and below this range the unit cutting energy follows the beta line very satisfactorily, while the Rockwell hardness for temperatures below 600° shows a rather inverse relation to beta and the unit cutting energy. It may be that this relation would not appear if some other type of machinability tests had been employed.

The results shown in Fig. 5, indicating a relation between the unit cutting energy and the Rockwell hardness, as influenced by the degree of cold drawing, also are interesting. From a percentage standpoint, the unit cutting energy is reduced but little for a much greater percentage increase in Rockwell hardness. For this reason, the illustration is apt to be misleading. The writer has found very little difference in machining properties of free-cutting brass bars of different sizes but of the same

analysis, the degree of cold working being an unknown.<sup>3</sup> These results have been confirmed in cutting steel screw stock,<sup>4</sup> in which S.A.E. 1112 and S.A.E. 1120 were furnished in two different sizes but the machining characteristics of each remained practically identical.

J. L. KIMBERLEY, Waterbury, Conn. (written discussion).—Mr. Morris has opened the field for an unlimited amount of important work. He is one of the first who have attempted to correlate machinability with our more familiar physical properties. Similar investigations carried on at the Scovill Mfg. Co. and Hammond Laboratory, Yale University, have resulted in somewhat different conclusions from those reported in Mr. Morris' paper.

The method for determining machinability which we used consisted of comparisons of the penetration of a  $\frac{1}{4}$ -in. dia. flat twist drill for a constant number of revolutions at constant speed and constant load. This method was described in detail by A. Kessner.<sup>5</sup>

Fig. 12 shows diagrammatically the essential details of the device described by Kessner. The constant loading is achieved by the circular arcs *A* and *B* which are segments of a circle with *O* as center; the constant speed by a constant-speed motor driving gear *C*; and the constant revolutions by an automatic shutoff. A curve of the drilling is taken on cylinder *F* and this curve serves as a basis for all calculations.

The percentages used as machinability measurements were derived by comparison of the test curves of the samples under consideration with the curves of specially prepared standard leaded rods which were accepted as 100 per cent machinable. The standards were made from a special alloy with the following limits: copper, 62 to 63 per cent; lead,  $2\frac{1}{2}$  to 3 per cent; zinc, remainder. The actual standards used were made from a billet whose composition was in the center of this range. One billet produced enough standards to last several years. The standards had a tensile strength of 50,000 lb. per sq. in. Certain specimens compared with them have shown more than 100 per cent machinability.

Machinability tests made on alloys of similar composition by the above method and by Mr. Morris' method indicate that machinability values derived by the two methods are comparable. Thus, results on Muntz metal (nonleaded) compared with free-turning brass rod by Mr. Morris' method gave a comparative machinability of 42

per cent for the nonleaded Muntz:  $\frac{10,490}{24,700} \times 100 = 42$  per cent. Results by the drill test method show 35 per cent machinability for the nonleaded Muntz.

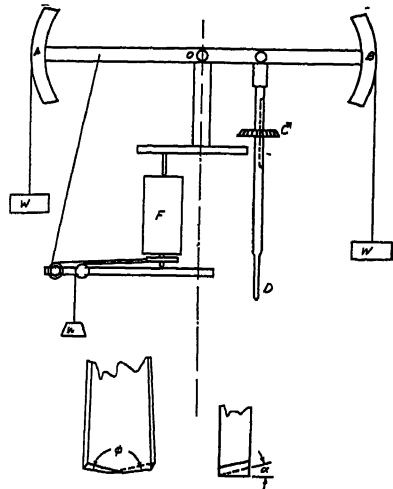


FIG. 12.—DETAIL OF DRILL D.

<sup>3</sup> Reference of footnote 2.

<sup>4</sup> O. W. Boston: Machining Properties of Some Cold-Drawn Steels. *Trans. Amer. Soc. Mech. Eng.* (1930) 53, MSF-53-6.

<sup>5</sup> *Carnegie Schol. Mem.* Iron and Steel Inst. (1913) 5, 10.

# MACHINABILITY OF FREE-CUTTING BRASS ROD

Mr. Morris has reported that "Machinability of annealed leaded brass rod is fully affected by the presence of beta." For each determination in his investigation of this point he has used quenched samples.

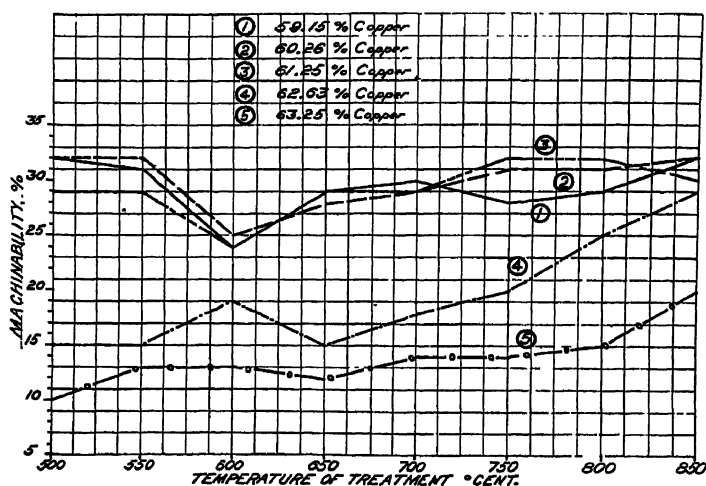


FIG. 13.—EFFECT ON MACHINABILITY OF INTRODUCING BETA INTO ALLOYS THAT NORMALLY HAVE LITTLE OR NO BETA AND OF INTRODUCING ADDITIONAL BETA INTO ALLOYS THAT HAVE BETA AT EQUILIBRIUM. FURNACE-COOLED SAMPLES.

It is interesting to note the variations in machinability which we obtained on non-leaded brasses when beta was introduced by suitable heat treatments. Fig. 13 shows

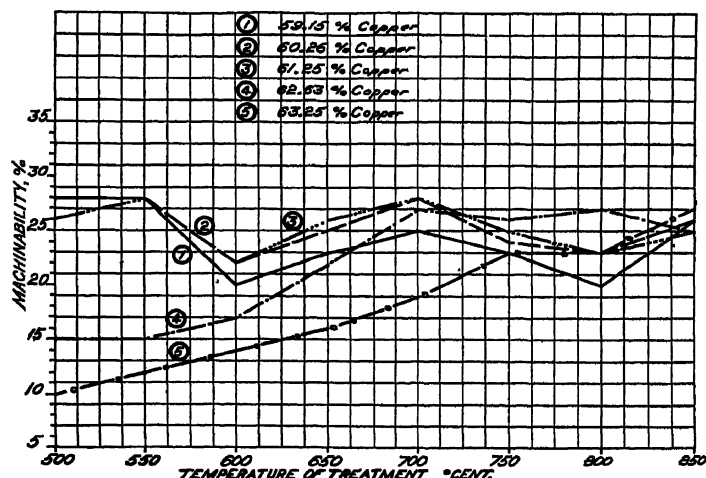


FIG. 14.—EFFECT OF HEAT TREATMENTS ON MACHINABILITY OF SOME ALLOYS AS IN FIG. 13, FOLLOWED BY AIR COOLING.

Effect on machinability of introducing beta into alloys which have normally little or no beta, and of introducing additional beta into alloys which have beta at equilibrium. All samples were all furnace-cooled. Alloys 1, 2 and 3 show a practically flat

machinability curve throughout the entire temperature range regardless of the amount of beta. Alloys 4 and 5 are low in machinability but show a decided improvement when beta is left in the alloys after slow cooling from the higher annealing temperatures.

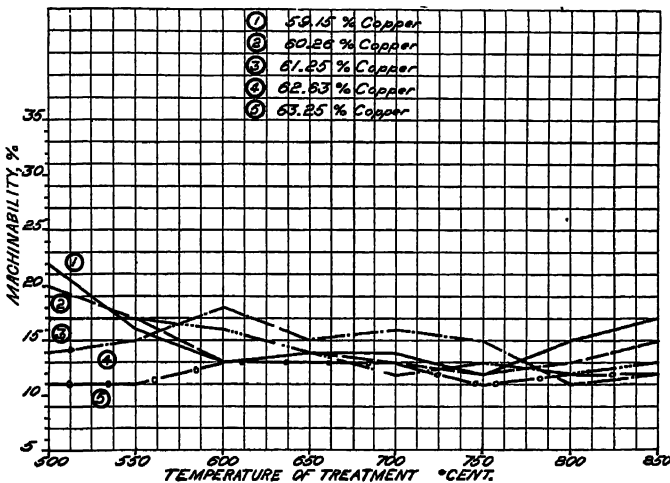


FIG. 15.—MACHINABILITY OF WATER-QUENCHED SPECIMENS.

Fig. 14 shows the effect on machinability of heat treatments of the same alloys treated at the same temperatures followed by air cooling. In alloys 4 and 5 more beta is retained after a low-temperature anneal followed by air cooling than would be the

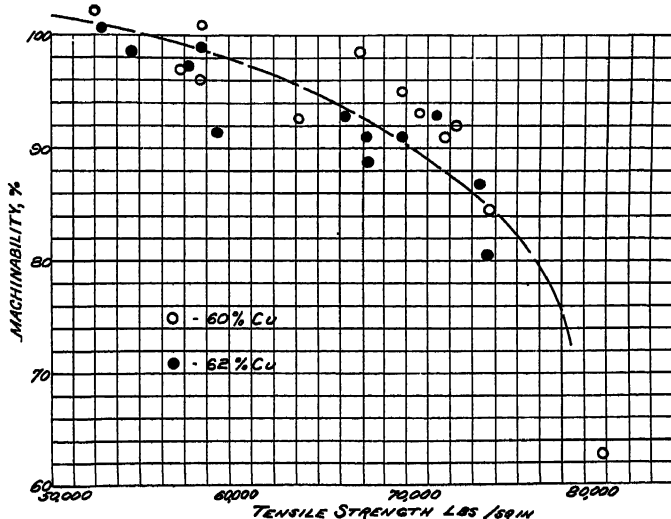


FIG. 16.—MACHINABILITY TESTS ON SAMPLES FROM SPECIALLY PREPARED RODS.

case with the same anneal followed by furnace cooling, and the improvement in machinability of air-cooled specimens therefore starts between 500° and 550° C.

Fig. 15 shows that water-quenched samples have poor machinability regardless of quenching temperature or amount of retained beta.

These results naturally suggest the possibility that Mr. Morris might have reached different conclusion with alloys which contained beta not produced by quenching.

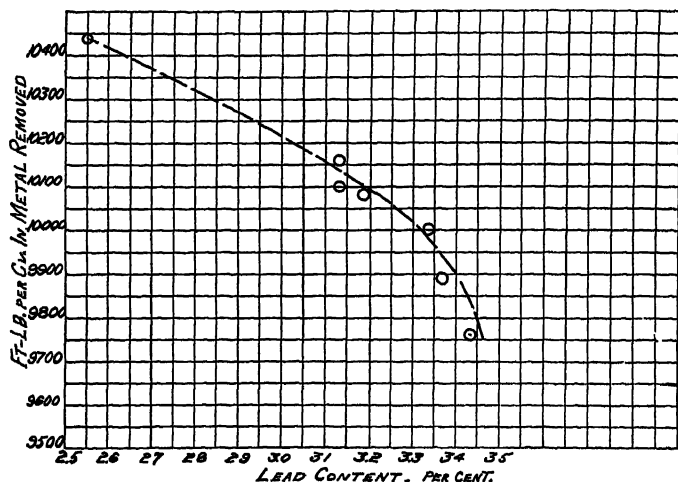


FIG. 17.—REPLOTTING OF A SECTION OF FIG. 3.

Mr. Morris' fourth conclusion, that "machinability is improved by cold drawing after annealing," recalls an interesting experiment which was made in our mills, automatic screw machine department and laboratory.

Two alloys were used, containing approximately 60 and 62 per cent Cu respectively with 3 per cent Pb in each case. These alloys were extruded and then processed, using three finish anneals (475° C., 550° C. and 650° C.) followed by four final reductions (approximately 15, 20, 25 and 30 per cent). All rods were finished on the same size. The tensile strengths varied from 52,000 to 81,000 lb. per sq. in. Machinability tests were made on samples from these rods, with the results shown in Fig. 16.

This figure illustrates two points. First, it confirms the opinion of Mr. Morris, that the copper content within the range of 60 and 62 per cent Cu in itself has little influence on machinability although the figure indicates that the alloy containing 60 per cent Cu, slowly cooled but still retaining beta, has slightly better machinability. Second, there is a definite downward trend in machinability with increased tensile strength.

These rods were then tested in a high-speed automatic screw machine, making a long threaded bushing. This involved hollow milling, forming, drilling and threading. Close observation at the machine and a study of the bushings and chips showed no differences in machinability until those rods having a tensile strength of approximately 70,000 lb. per sq. in. were reached.

At this point the chips began to come finer, the pieces cut were warmer, and the machine seemed to labor. On those samples with over 73,000 lb. per sq. in. tensile

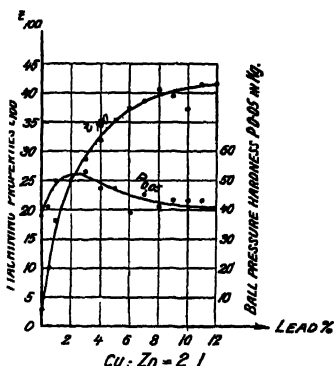


FIG. 18.—INFLUENCE OF LEAD PERCENTAGE ON BALL-PRESSURE HARDNESS AND MACHINING CAPACITY OF CAST BRASS (Kessner).



strength, the machine actually groaned and the chips were almost a powder. This experiment and our experience with free-turning rod complaints led to the following conclusion:

Cold working increases the energy required to cut free-turning brass rod, but soft metal cannot be cut efficiently without perfect support as in straight drilling. The soft rod will bend away from a side-cutting tool and chattering, digging in, nonuniformity in gage and short tool life will result.

Mr. Morris has plotted graphs (Figs. 2, 3, 4 and 5) to prove the validity of his conclusions.

The section of Mr. Morris' Fig. 3 from 2.5 to 3.5 per cent Pb, replotted to the same comparative scale as his other figures (Fig. 17), shows as radical a change in machinability as Figs. 2, 4 and 5. This replot indicates that additions of lead beyond 3.5 per cent would materially improve the machinability. Of course this increase in lead content could not be continued indefinitely, because the physical properties of the rod would be ruined eventually.

In Table 1 is shown the energy requirement with 25° rake tool, of tough-pitch copper as 12,450 ft-lb. per cu. in. and of free-turning brass rod as 8795 ft-lb. per cu. in., a difference of 3655 ft-lb. per cubic inch.

This indicates that a saving of even 1000 ft-lb. per cu. in. is of considerable importance in view of the difference in the actual machining of tough-pitch copper and free-turning brass rod. Mr. Morris' data, replotted as in Fig. 17, make such a saving seem very probable.

O. W. ELLIS, Toronto, Ont.—During the war considerable trouble was being experienced in the machining of certain parts for fuses. In order to circumvent these troubles, I was called upon to start an investigation on the machinability of brass rods and brass castings. As a matter of fact, the results which I obtained were found to be far less important in their effect upon machine shop practice than alterations which took place in the design of the machines. It was found, as was referred to by the last speaker, that instability in the machine tool may cause considerable differences in the apparent machinability of the materials being worked upon.

In the particular cases that I have in mind a circular slot had to be routed in a piece of brass and difficulty was experienced in keeping this slot to a constant width. The routing tool tended to swing backward and forward transversely within the slot as the slot was being made. That was overcome by making the machine more rigid.

However, we did discover that certain alloys were far better than others for machinability. The work that I did I shall refer to in a moment or two. Just now I want to show a curve that appeared in a paper to which reference has already been made, that by Kessner, who used the drill test for his investigations of these alloys. Fig. 18 shows the results of Kessner's work, indicating the increasing machinability of copper-zinc alloys containing a ratio of 2 of copper to 1 of zinc as the lead content of the alloys is increased. Mr. Morris' work gives one the impression that the effects of the first additions of lead are far more severe than would be judged from Kessner's work. I believe Mr. Morris to be more nearly correct in his conclusions and think that Kessner, for some reason or other, has not shown how very decided are the effects of these first additions of lead.

Mr. Morris has made no attempt in his paper, as far as I can see, to show how the machinability of brass is affected by its copper content. The experiments which I carried out in this connection were conducted under somewhat rough conditions. We used a modified Kessner test and made two determinations: (1) of the energy required to machine brass of varying compositions, and (2) of the machining time; *viz.*, the length of time taken to drill a hole of definite depth.

Fig. 19 shows the results of tests made on a series of brasses containing from 56 up to about 65 per cent Cu; as the copper content increases, the amount of power required to machine increases. In other words, as the alpha content of these alloys increases, the power required to machine increases.

In this connection there is one rather important point that I think one has to bear in mind. These tests were carried out, as I said, with a modified Kessner drill test. We found that certain alloys, as is well known, formed, as they were machined, long drillings which tended to clog the drill, but although in the alloys of low copper content we did not observe this effect, in the alloys of high copper content it was quite noticeable.

I am not sure how to explain the inversion in these curves between 57 and 59 per cent Cu. I think it has to do with the fact that within this range there is a tendency

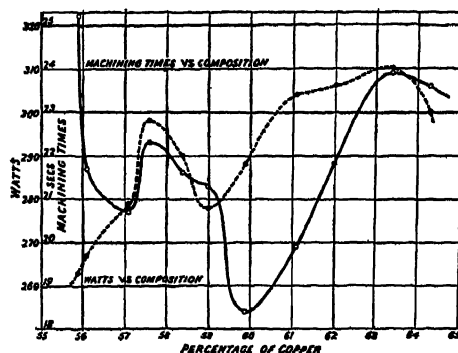


FIG. 19.—MACHINABILITY TESTS ON A SERIES OF BRASSES.

for short chippy turnings to be produced. It may have to do with the relative proportions of alpha and beta present in the alloy. The question of the type of chip, or the type of turning produced, was gone into very thoroughly. In cast alloys containing a greater percentage of zinc than 41, we found a tendency for long, thin, ribbon-like turnings to be produced, whereas in similar alloys containing less than 41 per cent Zn strong, spiral-shaped turnings are produced. Cast alloys containing about 41 per cent Zn tend to produce short, chippy turnings.

One other point—the question of the machinability of brass that has been cold-drawn. In a paper published in 1917 or 1918, I pointed out that the disposition of the microconstituents of brass had considerable effect upon its machinability. One important point brought out was that cold-worked 40 per cent Zn rods, having Brinell hardness numbers as high as 140, machined as readily as stampings and castings of similar composition having a Brinell hardness of approximately one-half that value.

I am not suggesting that there is any relationship between machinability and Brinell hardness. This, in fact, is made clear by the statement I have just made. This difference in machinability was shown to be due to the disposition of the alpha and beta constituents in the stampings, castings or drawn rods, respectively.

In stampings and castings, the matrix of the beta constituent generally contained crystals of the alpha constituent possessed of no definite orientation and so disposed that similar types of structure were to be observed across whatever section of the piece might be cut. In rod, however, the structure varied according to whether sections normal to, or parallel to, the axis of the rod were taken.

It is especially noteworthy that in sections parallel to the axis of such rods almost continuous crystallites of the beta constituent may be observed. It is this fibrous structure that appears to enhance the machinability of brass. Desch has carried the

investigation of the effect of fibrous structure on the machinability of brass somewhat further and has shown that an arrangement of fine fibrous alpha crystals, separated by a comparatively small quantity of beta, is the most desirable for machining purposes.

W. B. PRICE, Waterbury, Conn. (written discussion).—In connection with Mr. Morris' statement that "no tests have as yet been made to determine the effect of the usual impurities, such as tin and iron," it may be interesting to record some experiments we made with high-speed rod, adding known amounts of iron and nickel but no tin. Some 50,000 lb. of material was cast and rods of the following sizes were produced:  $\frac{3}{16}$  in. hex.,  $\frac{3}{16}$  in. square; 0.436, 0.350, 0.250 and 0.101 in. round. Variations in chemical composition of this rod were as follows:

	PER CENT
Copper.....	59.53-60.76
Lead....	3.03- 3.72
Iron.....	0.28- 0.60
Tin.....	none
Nickel....	0.51- 0.84
Zinc.....	remainder

The tensile strength of this material ranged from 64,600 to 65,500 lb. per sq. in. Test runs with this material on the 00 B. & S. high-speed machines, running at 5000 r.p.m. on knurled thumb nuts, indicated that it machined as well if not better than our standard high-speed rod. On the  $\frac{3}{16}$ -in. square, there was some mechanical difficulty in putting this material through the standard breaking down reductions, which undoubtedly was due to the abnormally high iron content. These tests were repeated with the addition of about 0.25 per cent Sn, with equally satisfactory results.

These tests indicated that satisfactory high-speed rod could be produced from material having the following composition: Cu, 59 to 61 per cent; Pb, 3 to 4; Sn, max., 0.20; Fe, max., 0.20; Ni, 0.50; Zn, remainder. In Germany, high-speed rod of the following composition is used: Cu, 58 per cent; Pb, 2.5 to 3.5; Zn, remainder. They claim that extensive research shows that this composition gives better results than the standard mixture used in this country. They use 100 per cent scrap, no copper and add only a little zinc. A typical 880-lb. charge would contain turnings, 33 per cent; solid scrap, 67 per cent; enough zinc to balance mixture.

D. K. CRAMPTON, Waterbury, Conn. (written discussion).—As Mr. Morris himself says, the term "machinability" is not well defined; nor is it clearly apparent whether power, finish, tool life or some other consideration should be taken as the main criterion. From a purely technical standpoint, the power consumed in removing a certain volume of metal would seem to be the most logical criterion. From a practical standpoint, however, tool life is much more important. The question of finish is intimately bound up with tool life and should be considered as one of the factors entering into it. In practice the actual power consumed is a rather negligible part of the total cost.

Tool life, however, is of paramount importance. Not only is the initial cost of tools and their upkeep apt to be high, but the delay time due to necessity for regrounding and new setups is very expensive. We believe, therefore, that power consumption per unit volume of metal as used here is important only if it can be shown that it reflects tool life directly.

Mr. Morris makes the statement based on a comparison of a single nonlead brass of 66.6 per cent Cu and another of 60.7 per cent Cu that variation of copper is rather unimportant. This finding does not check at all with general service experience, where the difference in the copper content within the range of alloys usually extruded makes a pronounced difference in performance, the higher copper being decidedly the better. In some long-time production tests on automatic screw machines a decidedly

different result was found. In the test in question a standard high-speed screw machine was used, making a standard production article from rod of about  $\frac{5}{8}$  in. dia. Fabrication called for four cutting operations: a form, drill, chamfer and cutoff. Lots of approximately 10,000 lb. each were carefully prepared, each lot having certain definite physical and metallurgical characteristics. From each lot approximately 250,000 parts were made, so that any minor variations of material, tools, setup, etc., were largely eliminated. The criterion used was the number of pieces obtained per grind for each tool. In two of the lots a direct comparison could be obtained between a material of Cu, 62.27 per cent and Pb, 4.06 per cent and Cu, 60.06 per cent and Pb, 4.11 per cent. The average increase in tool life with the higher copper alloy over the lower was more than 30 per cent.

Fig. 3 is interesting. Several years ago in our laboratory we ran tests on the effect of lead on cutting properties. At that time an ordinary power hack saw was used with a given load setting and the time required to saw through a rod of given size was taken. The curve of time versus lead content follows remarkably closely that given in Fig. 3, except that we did not get so pronounced a knee in the curve as Mr. Morris did. In addition, in the large-scale screw machine tests referred to above we also had a direct comparison between two lots of rod, one having an analysis of 62.27 per cent Cu, 4.06 per cent Pb and the other 62.26 per cent Cu, 3.41 per cent Pb. The higher lead content rod gave a 15 per cent greater tool life than the lower. It should be pointed out, however, that a lead content over 4 per cent is not commercially practical, as difficulties are encountered with fabrication of the rod and there is a slight falling off of physical properties.

Fig. 5 is interesting because it shows results contrary to those usually found. The present tests indicate that increase of hardness by cold drawing decreases the energy per cubic inch of metal removed; in other words, increases machinability. It is well known that in the use of free-turning rod in screw machines, especially in the smaller sizes, a hard rod performs markedly better than a softer rod. This we have always attributed not to any superior cutting properties per se but rather to the fact that a harder, stiffer rod stood up against the tool better, resulting in an apparent improvement in machinability. We had not heretofore made thorough tests to find out what the relative cutting properties were apart from this question of standing up against the tool. Since receiving this paper we have made some hurried tests using the hack-saw method referred to above, as well as a high-speed drill test. With both types of tests we find that, with identically the same rod, annealed material showed about a 13 per cent improvement in machinability over one drawn 24 per cent reduction of area. It is, therefore, hard to reconcile the data presented in Fig. 5.

Entirely apart from the question of the accuracy of the data presented, it is interesting to consider the matter from a somewhat different viewpoint than that taken by the author. Let us consider the effect of the various factors over the range in which they might normally vary in commercial practice. Assume that commercial free-turning screw machine rod might show the following range of properties: copper content, 60 to 63 per cent; lead content, 3 to 3.75 per cent; final reduction by cold drawing, 20 to 30 per cent; beta, 10 to 50 per cent. From Mr. Morris' data the change in energy consumption due to such range of copper would be approximately 6 per cent; that due to the variation in lead content would be approximately 6.5 per cent; that due to the variation in hardness, 2.5 per cent; that due to the variation in beta content, 2 per cent. Assuming that his values are correct, this would indicate that these factors, as they usually vary in practice, would be rated in the following order of importance: (1) variation in lead content; (2) variation in copper content; (3) variation in hardness; (4) variation in beta content.

A. MORRIS (written discussion).—When one considers the number of variables influencing the results of any machining operation on free-cutting brass rod, and the scarcity of literature on the subject, it is small wonder that we find such divergence of opinion as there appears to be among persons who have given the subject most thought. However, when we have a sufficiently comprehensive picture, each of these apparently conflicting views will fall into its proper place and many seeming contradictions will disappear.

The very interesting results of Dr. Ellis on the machinability of low-leaded Muntz metal check with those of Mr. Kimberley on non-leaded brass, and both are in agreement with many tests the author has made on this type of material. Here beta seems to aid materially, probably because the presence of the brittle constituent causes the chips to break up more readily. (See Fig. 20.)

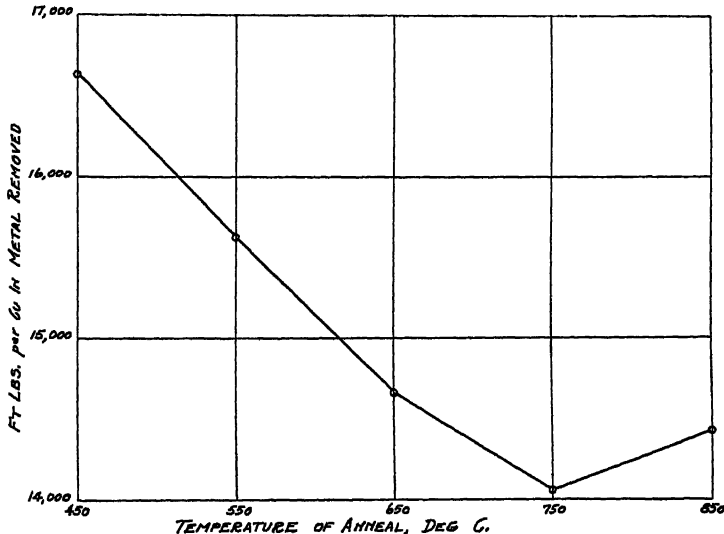


FIG. 20.—VARIATION OF UNIT CUTTING ENERGY OF LOW-LEADED MUNTZ METAL WITH ANNEALING TEMPERATURE.

In the highly leaded rod, however, its influence is quite the reverse, perhaps because the chips break up readily in any case on account of the lead. This would also explain the apparent conflict between Mr. Kimberley's results and the views of Mr. Crampton on the influence of copper content.

Mr. Kimberley has called attention to the fact that the author used quenched samples in obtaining the results plotted in Fig. 4. Similar tests made with both quenched and air-cooled samples show that though the air-cooled samples are softer and machine more readily than do the quenched, the upward trend of the curve toward the right is marked (Fig. 21).

The results shown in Mr. Kimberley's Fig. 5 are difficult to analyze, since degree of anneal and amount of drawing are varied simultaneously. However, it seems reasonable to assume that the rods showing highest tensile strength are those containing most beta. The range over which the cold working has been varied is not very great. It is possible that the ill effect of the beta is sufficient to more than counterbalance the beneficial effect of cold drawing. A great deal would also depend on the orientation of the sample during the machinability test. As Dr. Ellis has pointed out, drawn rod exhibits distinctly directional machining properties.

Fig. 22 shows the results of tests made on samples of free-cutting rod in four different conditions, as follows:

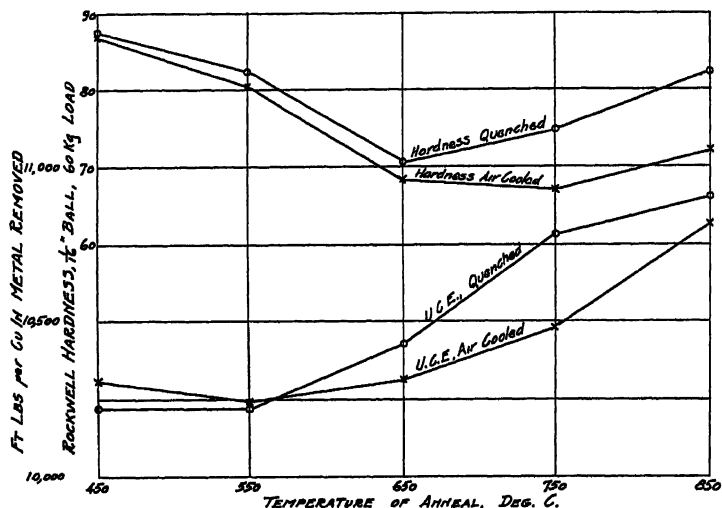


FIG. 21.—INFLUENCE OF ANNEALING TEMPERATURE ON UNIT CUTTING ENERGY AND HARDNESS OF QUENCHED AND AIR-COOLED SAMPLES.

1. Rod containing about 5.0 per cent beta, drawn 36.0 per cent hard.
2. Same rod annealed 2 hr. at 500° C., 3.0 per cent beta.

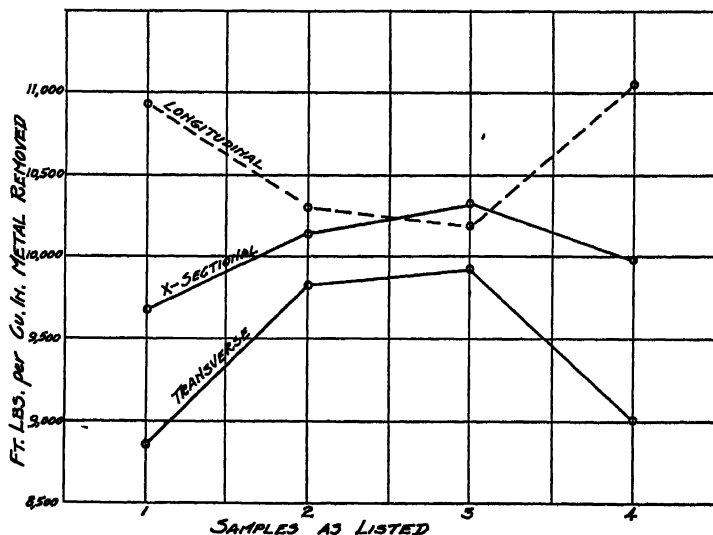


FIG. 22.—DIRECTIONAL CUTTING PROPERTIES OF FREE-CUTTING BRASS ROD AS INFLUENCED BY DRAWING AND ANNEALING.

3. Same rod annealed 8 hr. at 500° C., no beta.
  4. Same rod annealed 8 hr. at 500° C., drawn 34.0 per cent hard, no beta.
- Three tests were made on each sample, as follows:
1. Cuts parallel to axis of rod (longitudinal).

2. Cuts perpendicular to axis of rod, on a plane parallel to axis (transverse).
3. Cuts on cross-section of rod, perpendicular to axis (cross-sectional).

All tests reported in the paper were of the cross-sectional type.

Each point plotted represents the average of tests made on three different rods prepared in the same manner. The results show that:

1. Hard-drawn rod exhibits distinct directional properties, which, though diminished, still persist after annealing.
2. A completely homogenized rod has a slightly higher unit cutting energy than one which still contains a very small amount of beta.
3. The directional properties do not depend on the presence of beta.
4. Transverse and cross-sectional cuts are more easily made on hard-drawn than on annealed rod. Since practically all screw-machine operations are of these types, we have here confirmation of conclusion 4 of the paper. The longitudinal cut is affected adversely by drawing.

It seems possible that these changes may be causally related to crystallographic orientation due to drawing.

In Fig. 17 Mr. Kimberley has replotted the high-lead end of Fig. 3, using a large vertical scale. In so doing he has taken a step which the author hesitated to take, feeling that the downward trend of the last five points on the curve was most likely accidental. Some tests made on rod containing about 4.0 per cent lead fall on the continuation of the curve as drawn in Fig. 3.

Professor Boston and Mr. Hartman point out various theoretical sources of error. The author has not been unmindful of these, but has found that practically their influence is insufficient to cause serious variations in the results. Tests on series of samples fall on a smooth curve, even when the difference between the samples is slight and the vertical scale used is large, as shown in Figs. 2, 3, 4 and 5. Under these conditions very small errors would cause distinct scattering of the points. The results obtained are more coherent than those of any other machinability test with which the author is familiar.

It is surprising that Fig. 2 should have caused so much comment. It was included only as an indication that the results of any such test as this must be considered as purely comparative. In discussing this figure, Professor Boston and Mr. Hartman agree that the increase in cutting energy with increase in depth of cut is due to side friction. Mr. Hartman also suggests that the rise below 0.023-in. cut is due to energy lost by the tool sliding over the surface of the sample without removing metal. While no explanation was offered in the paper, the author felt that the up-turn below 0.023 in. was caused by the energy losses inherent in the test becoming relatively large.

Professor Boston has analyzed the results shown in Fig. 5 from a percentage standpoint. Any such analysis is apt to be misleading, because of the nature of the Rockwell scale. A difference of 1 per cent in Rockwell number in the range, say, from 50 to 60, corresponds to a much smaller change in actual hardness than does a similar difference in Rockwell number in the range from 90 to 100. In Fig. 5 the vertical scales were chosen to bring out the point that the two curves sloped in opposite directions. It is understood that the degree of slope of either one is purely the result of arbitrary choice of vertical scale.

The author has no data on the speed of cutting to offer Mr. Hartman. It has been assumed that in the comparative tests reported the speed of cutting remained practically constant.

The importance of the form of the chip is well emphasized by Mr. Hartman, and is also mentioned by Dr. Ellis. The chips from the free-cutting brass rod samples all broke up to about the same extent. It was not until the lead content dropped to about 0.5 per cent that occasional chips failed to break up.

Mr. Crampton and Professor Boston stress the importance of tool life. Mr. Crampton believes that unit cutting energy is important only in so far as it reflects tool life. This is one of the assumptions on which the present work is based, and it seems a reasonable one. In performing a given machining operation, a tool is called upon to do more work on a rod whose unit cutting energy is high. More heat must be dissipated. The cutting pressures must be higher. It seems logical, then, to assume that the tool life will be shortened.

In large-scale test Mr. Crampton found that rod containing 62.27 per cent of copper showed 30.0 per cent longer tool life than rod having only 60.06 per cent of copper. A 60.0 per cent rod produced under mill conditions would expectably have more beta than one containing 62.25 per cent of copper. If we consider his experience in this light, it confirms the author's conclusion regarding the influence of beta. On the other hand, it would seem from Mr. Price's remarks that he does not altogether share Mr. Crampton's view that high-copper rod is better than low-copper rod.

Both Mr. Kimberley and Mr. Crampton find it difficult to reconcile the conclusion regarding the effect of drawing with their own convictions. Fig. 22 throws more light on the nature of this phenomenon.

Mr. Crampton has suggested an interesting quantitative arrangement of the various factors. The author feels this may be a little premature, in the absence of a more complete study of the influence of copper content. Some of his assumptions are also open to question.

Mr. Price's remarks concerning the influence of impurities are most interesting. Work on the effects of small quantities of tin and iron is progressing, as well as some tests on samples containing various amounts of copper. The author hopes to deal with these points in a later paper.



## Effect of Small Percentages of Certain Metals upon the Compressibility of Lead at an Elevated Temperature

BY LYALL ZICKRICK,\* SCHENECTADY, N. Y.

(New York Meeting, February, 1932)

NUMEROUS brands of virgin pig lead are used in the manufacture of lead and lead-alloy cable sheath for commercial cables. In changing from one brand of pig lead to another a readjustment of press operating conditions is nearly always necessary. This is due largely to different flow characteristics, and some brands extrude at a much lower pressure than others; for example, copper-bearing lead requires much more pressure than a low-bismuth lead under the same operating conditions.

With the modern type of lead press the extrusion practice in general differs very little. Molten lead at a temperature of 375° to 400° C. (710° to 750° F.) is cast in a water-cooled cylinder and allowed to cool or solidify into a slug for six to nine minutes. This slug is forced into the die block and around the core tube through which the cable runs. The die block is held at an optimum temperature by means of gas flames, usually 175° to 225° C. (350° to 435° F.). Measurements of the temperature of the cable sheath taken at the time of extrusion have covered a range of 190° to 225° C. (375° to 435° F.). According to Tammann, the rate of extrusion for a metal under constant pressure through a simple orifice is almost doubled for each 10° C. rise in temperature. Because of the irregularity of die-block construction, such a great increase is not obtained in lead-cable extrusion practice.

To obtain more definite information about the effect of small percentages of metals usually present as impurities in virgin pig lead, a series of compression tests were made covering several different brands of lead and various alloys. Since the usual temperature of the sheath is approximately 200° C. as it emerges from the die block, these compression tests were all performed at 200° C.

Five different brands of virgin pig lead were selected, as follows:

Brand A: A desilverized western lead of very high purity. This lead contains neither copper nor bismuth.

Brand B: A bismuth-free southeastern Missouri lead, usually containing 0.05 to 0.08 per cent copper.

Brand C: A copper-free mid-western desilverized lead of very good grade, usually containing around 0.06 to 0.10 per cent bismuth.

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\* Research Laboratory, General Electric Co.

Brand D: A copper-free desilverized lead of very good grade, refined by the Harris process, usually containing from 0.07 to 0.12 per cent bismuth. After desilverizing, this lead is treated with chlorine to remove the zinc.

Brand E: A bismuth-free southeastern Missouri lead which has been desilverized. This lead contains no copper.

The bismuth and copper content (as determined by chemical analysis) of the particular pigs of lead selected for use were as shown in Table 1.

TABLE 1.—*Analyses of Pigs Used*

Brand	Cu, Per Cent	Bi, Per Cent	Sn and Sb, Per Cent
A	b	b	b
B <sup>a</sup>	0.07	b	b
C	b	0.098	b
D	b	0.082	b
E	b	b	b

<sup>a</sup> Spectrographic analysis of Brand B showed silver to be present.

<sup>b</sup> Either none or a trace detectable by spectrographic analysis.

To obtain additional information regarding the chemical composition of these leads, the suppliers were asked to give the average complete analysis of each particular brand. These analyses are given in Table 2.

TABLE 2.—*Analyses of Brands of Lead Used*

Composition, Per Cent	Brand A	Brand B	Brand C	Brand D	Brand E
Cu	Tr.	0.063	0.0005	0.0006	Tr.
Bi	0.0025	None	0.12	0.08 to 0.095	None
Sb	} 0.003	} Tr.	0.005	0.0007	} Tr.
As			Tr.	None	
Fe	0.001	Tr.	Tr.	0.0008	Tr.
Zn	0.001	Tr.	0.003	0.0005	Tr.
Cd		0.001			0.002
Ni-Co		0.004			Tr.
Ag	Tr.	0.009	16 oz. per ton	0.00056	Tr.

#### PREPARATION OF SPECIMENS AND METHOD OF TESTING

All specimens were prepared and tested in exactly the same manner, so as to be directly comparable. As the sheath in lead press extrusion is formed from a cast slug, the specimens for compression tests were taken from cast slugs. These slugs were about 11 in. long and measured 2 by 1 in. in cross-section. To prevent oxidation during melting, all

melts were made in a hydrogen furnace. A clean graphite crucible was used and the charges were cast in a warm iron mold.

In the preparation of alloys (the 0.035 per cent calcium alloy excepted) the alloying element was wrapped in sheet lead of the same brand as the charge, immersed in the molten metal and thoroughly stirred until all in solution. The 0.035 per cent calcium alloy was prepared by adding the requisite amount of a 1 per cent calcium-lead alloy that had been made electrolytically. A higher temperature was used in the preparation of the copper series than in preparation of the other alloys. As the furnace atmosphere was hydrogen, no oxidation could take place. All charges were thoroughly stirred just before pouring.

Specimens for test were cut from the lower portion of the slug and carefully machined to size, 0.75 by 0.75 in. by 1.50 in. long. A specimen before test and after test is shown in Fig. 1.

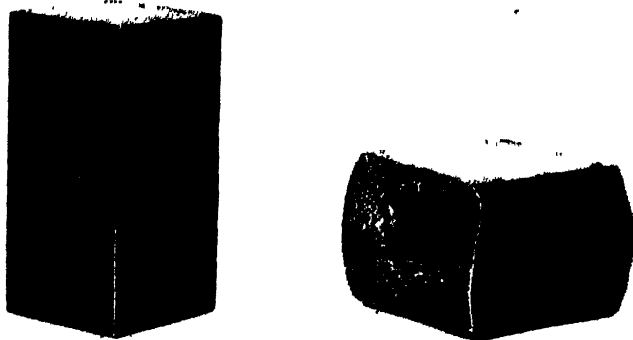


FIG. 1.—REPRESENTATIVE TYPE OF LEAD SPECIMEN BEFORE AND AFTER DEFORMATION.

All the specimens were tested in an oil bath maintained at a temperature of 200° C. by two immersion electric heaters. The oil bath was placed in an Olsen testing machine and the specimen immersed in the hot oil between steel plates. The end of a thermometer rested in direct contact with the specimen. The head of the testing machine was brought down to make contact with the plate, which rested on top of the specimen, and the beam placed at zero load. The specimen and plates were allowed 30 min. to come to an even temperature. During the test the deformation was measured by means of a 1-in. Federal dial gage which measured to  $\frac{1}{1000}$  in. The speed of the machine was held exactly the same for all specimens: 0.05 in. per 1.5 min. Readings were taken every 1.5 min. for each 0.05-in. deformation.

#### LEADS AND LEAD ALLOYS TESTED

The results of these deformation tests may best be studied by arranging the data in groups, as follows:

Group I. The five brands of virgin pig lead.

Group II. Brand A lead alloyed with varying amounts of copper ranging from 0.02 to 0.50 per cent.

Group III. Brand A lead alloyed with varying amounts of bismuth ranging from 0.50 to 1.0 per cent.

Group IV. (a). A comparison of brand A and brand B lead, each alloyed with 1 per cent Sb and 2.25 per cent Sn. These are commercial cable-sheath compositions. (b). In this group are included data on brand A lead alloyed with 0.035 per cent Ca, and brand A lead alloyed with 0.25 per cent Cd, 1.5 per cent Sn, representing cable-sheath compositions which are more or less new.

Group V. A series of tests performed at different temperatures on specimens prepared from brand D virgin pig lead.

In the tables that accompany each group the values represent the average of three determinations. Two of the determinations were performed in sequence. The third sample of each set was tested separately after all other samples had been tested. In all cases the separate values deviated very little from the average value. Temperature of the oil bath at the start and finish of the test is recorded.

### GROUP I

The composition of the five brands of virgin pig lead represented has already been given. In Table 3 are the results of the compression tests.

TABLE 3.—*Results of Compression Tests on Group I*

Deformation, In.	Load, Lb. Average of Three Determinations				
	Brand A	Brand B*	Brand C	Brand D	Brand E
0.15	203	425	242	228	210
0.25	225	435	270	250	232
0.35	246	535	296	275	250
0.45	273	580	326	300	280
0.55	313	635	370	340	310
0.65	368	705	428	385	352
0.75	430	770	502	455	415
TEMPERATURE, DEG. C.					
Start.....	200	200	200	200	200
Finish.....	191	197	197	199	200

\* Average of five determinations.

The figures of Table 3 plotted as curves are shown in Fig. 2. The copper-bearing lead, brand B, required more pressure to deform than

any of the other leads. In this particular test the values run approximately 75 per cent higher. Brands A and E, which are of very high purity and contain neither bismuth nor copper, are the softest, and brands C and D, which contain bismuth, require only slightly more pressure to deform.

Particular attention is called to brand E, which is a southeastern Missouri lead that has been desilverized. Desilverizing greatly softens this lead, as may be seen by comparing the deformation pressure for

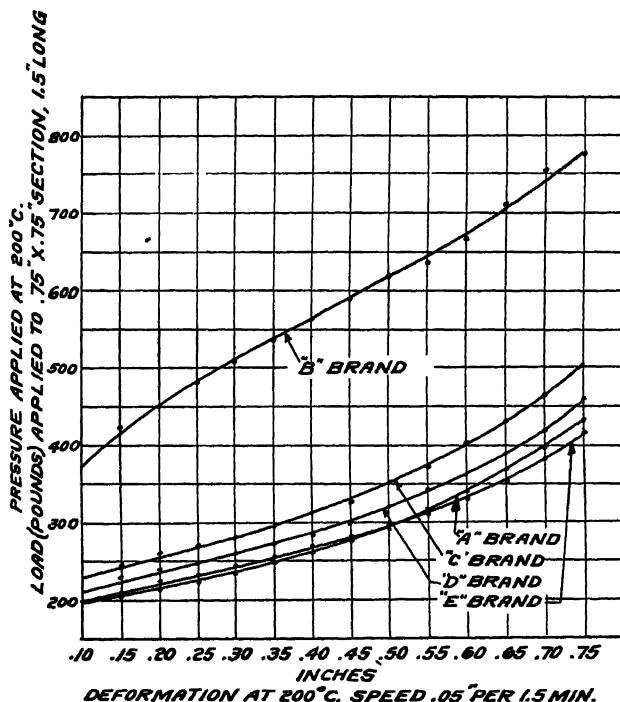


FIG. 2.—DEFORMATION PRESSURES REQUIRED FOR DIFFERENT BRANDS OF PIG LEAD.

brand E lead with brand B. Curves for brand E and brand A almost coincide. Although they represent leads from different parts of the country, they possess the same deformation characteristics after refining and desilverizing. Both are free from bismuth and copper.

## GROUP II

In group II, brand A lead has been used as a base and alloyed with copper ranging from 0.02 to 0.50 per cent. In Table 4 are tabulated the results of compression tests for this group.

The figures of Table 4 plotted as curves are shown in Figs. 3, 4 and 5. These curves show that the strengthening or stiffening effect of copper becomes pronounced as the amount is increased from zero to 0.08 per

TABLE 4.—Results of Compression Tests on Group II

Deformation, In.	Load, Lb. Average of Three Determinations								
	Brand A Lead	Percentage of Copper							
		0.03	0.06	0.08	0.1	0.2	0.3	0.4	0.5
0.15	203	332	412	442	433	436	408	450	468
0.25	225	370	436	455	468	492	438	496	513
0.35	246	408	472	485	513	530	475	532	558
0.45	273	448	513	530	562	583	515	578	598
0.55	313	495	563	582	623	653	568	636	650
0.65	368	556	632	655	680	733	636	712	735
0.75	430	642	723	755	766	816	743	820	845

TEMPERATURE, DEG. C.

Start....	200	200	200	200	200	200	200	200	200
Finish...	191	199	200	199	196	197	193	196	195

PERCENTAGE OF COPPER BY ANALYSIS

	0.02	0.05	0.09	0.11	0.20	0.28	0.41	0.50
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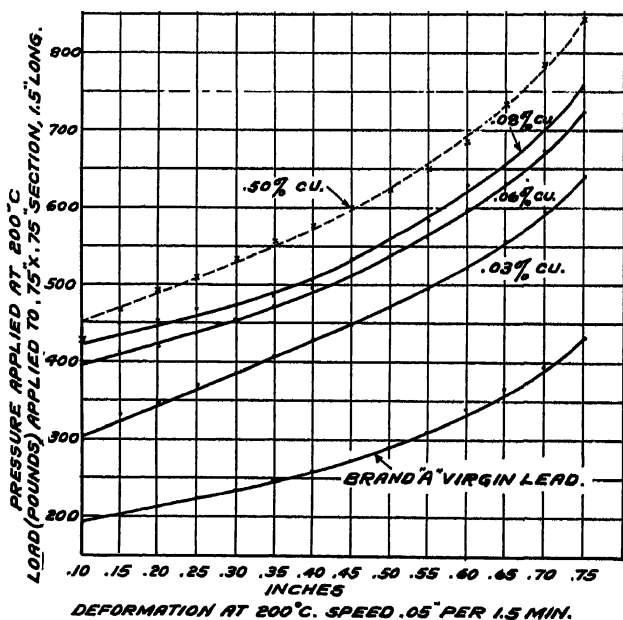


FIG. 3.—EFFECT ON BRAND A LEAD OF INCREASING COPPER CONTENT UP TO 0.08 PER CENT. ADDITIONAL COPPER TENDS TO SEGREGATE.

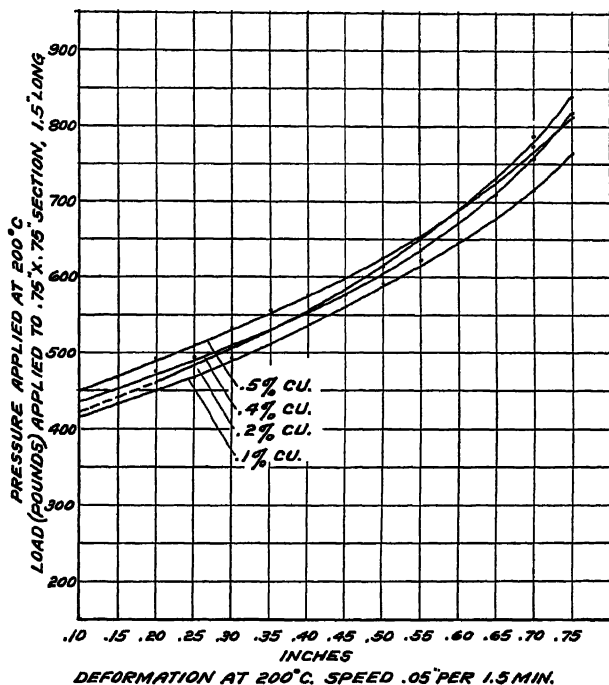


FIG. 4.—EFFECT OF ADDITIONAL COPPER ON BRAND A LEAD.

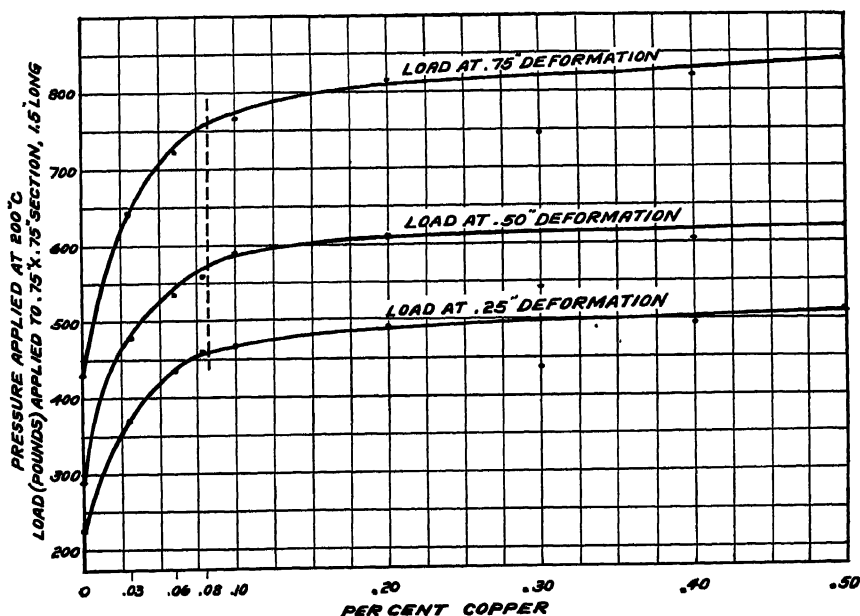


FIG. 5.—EFFECT ON BRAND A LEAD OF INCREASING COPPER CONTENT.

Up to 0.08 per cent Cu effect is pronounced because of formation of eutectic; beyond 0.08 per cent the copper tends to segregate.

cent. As copper and lead form a eutectic at 0.06 per cent Cu, 0.08 per cent Cu represents an alloy containing the maximum amount of this constituent with probably a slight excess of copper. Beyond 0.08 per cent Cu, the rate of increase in deformation pressure is of very small magnitude. Copper present in these greater amounts tends to segregate and consequently does not produce the stiffening effect that is caused by eutectic formation. Fig. 5 clearly pictures the effect of increasing copper content. Here, as shown in Fig. 2, the pressure required for deformation is almost doubled by the addition to pure lead of 0.08 per cent Cu.

### GROUP III

In group III, brand A lead has been used as a base and alloyed with bismuth ranging from 0.05 to 1.00 per cent. In Table 5 are the tabulated results of compression tests for this group.

TABLE 5.—*Results of Compression Tests on Group III*

Deformation, In.	Load, Lb. Average of Three Determinations						
	Brand A Lead	Percentage of Bismuth <sup>a</sup>					
		0.05	0.10	0.15	0.25	0.50	1.00
0.15	203	225	232	230	245	262	313
0.25	225	245	253	256	270	290	348
0.35	246	267	282	286	298	333	388
0.45	273	290	312	312	330	366	418
0.55	313	326	353	350	388	405	462
0.65	368	375	405	400	452	466	528
0.75	430	435	465	443	532	540	620

TEMPERATURE, DEG. C.							
Start.....	200	200	200	200	200	200	200
Finish.....	191	200	196	194	196	197	196

<sup>a</sup> Bismuth content checked by spectroscopic analysis.

Figures of Table 5 plotted as curves are shown in Figs. 6 and 7. These curves show that the pressure required for deformation gradually increases as the bismuth content increases. Fig. 7 best illustrates the effect of increasing bismuth content. The effect of bismuth is by no means as pronounced as the effect of copper.

### GROUP IV

In group IV<sub>a</sub>, brand A and brand B leads have both been alloyed with 1 per cent Sb, and 2.25 per cent Sn. In Table 6 are tabulated results of compression tests for this series.



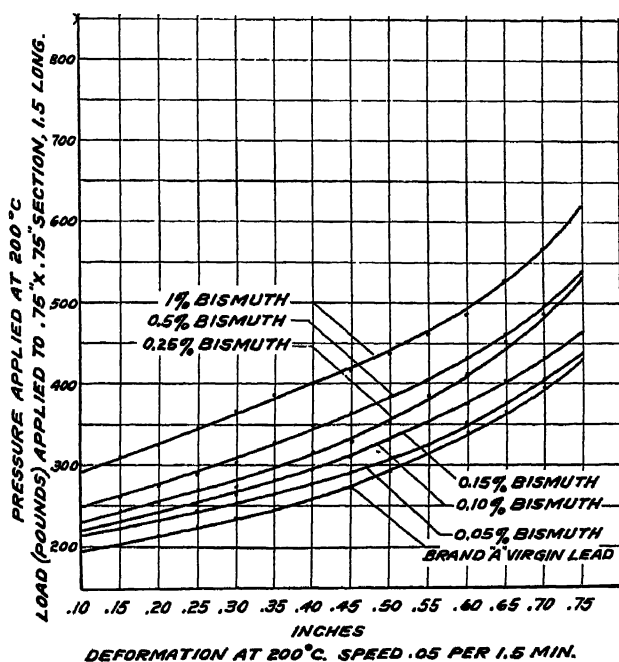


FIG. 6.—SLIGHT INCREASE IN DEFORMATION PRESSURE CAUSED BY ALLOYING BRAND A LEAD WITH BISMUTH.

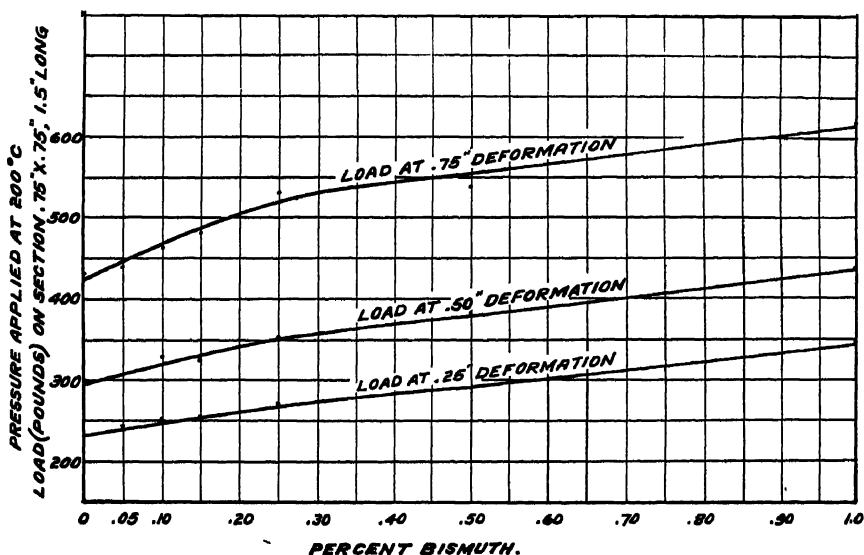


FIG. 7.—SLIGHT INCREASE IN DEFORMATION PRESSURE CAUSED BY ALLOYING BRAND A LEAD WITH BISMUTH.

TABLE 6.—*Results of Compression Tests on Group IVa*

Deformation, In.	Load, Lb. Average of Three Determinations					
	Brand A Lead			Brand B Lead		
	Pure	Sb, 1 Per Cent	Sn, 2.25 Per Cent	Pure	Sb, 1 Per Cent	Sn, 2.25 Per Cent
0.15	203	483	495	425	452	505
0.25	225	582	580	485	545	586
0.35	246	658	625	535	610	646
0.45	273	738	680	580	670	718
0.55	313	832	750	635	733	795
0.65	368	928	835	705	818	913
0.75	430	1093	960	770	926	1050
TEMPERATURE, DEG. C.						
Start.....	200	200	200	200	200	200
Finish.....	191	196	197	197	200	200

The figures of Table 6 plotted as curves are shown in Figs. 8 and 9. Data for brand A lead (a western desilverized lead, copper and bismuth free) are shown in Fig. 8, and data for brand B lead (a southeastern Missouri copper-bearing lead) are shown in Fig. 9. Fig. 8 shows that both tin and antimony appreciably harden or stiffen brand A lead, while as shown in Fig. 9, tin or antimony alloyed with brand B lead does not effect such a great change. The deformation pressures of the tin and antimony alloys made from these leads differ very little, however, regardless of the brand used.

TABLE 7.—*Results of Compression Tests on Group IVb*

Deformation, In.	Load, Lb. Average of Three Determinations		
	Brand A Lead	With 0.035 Per Cent Ca	With 0.25 Per Cent Cd, 1.5 Per Cent Sn
0.15	203	395	495
0.25	225	455	583
0.35	246	502	642
0.45	273	552	722
0.55	313	613	815
0.65	368	696	932
0.75	430	806	1083
TEMPERATURE, DEG. C.			
Start.....	200	200	200
Finish.....	191	199	196

In group IVb are included two alloys, made with brand A lead, which are somewhat new for use as cable sheath, 0.035 per cent Ca alloy, and 0.25 per cent Cd, 1.5 per cent Sn alloy. The compression test results are tabulated in Table 7.

The figures of Table 7 plotted as curves are shown in Fig. 10. In both cases the alloying constituents have appreciably increased the

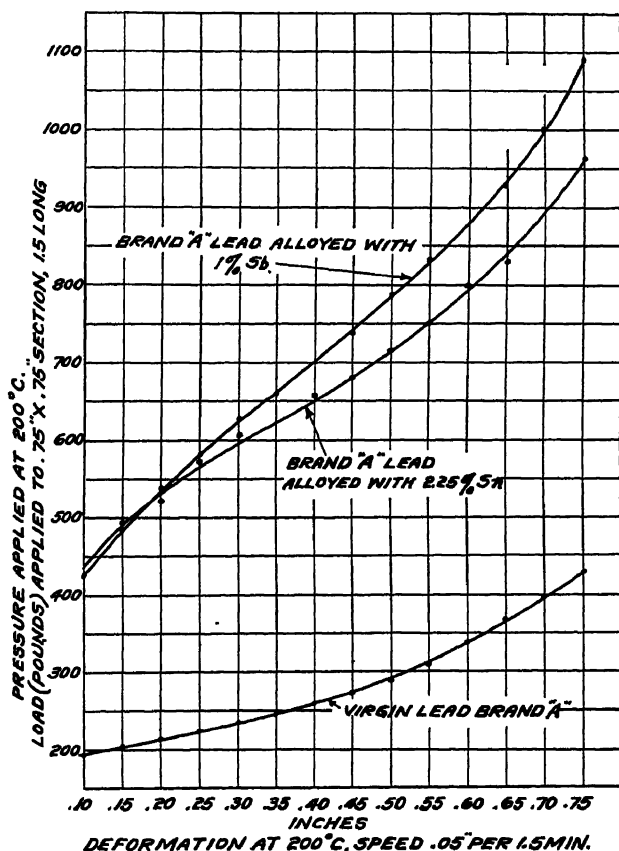


FIG. 8.—PRESSURES REQUIRED FOR VARIOUS ALLOYS OF BRAND A LEAD.

pressure required for deformation. The cadmium-tin addition has more than doubled the pressure required for brand A virgin lead.

## GROUP V

In group V test specimens taken from brand D virgin lead have been subjected to the compression test at different temperatures. These tests were run in order to tie in the effect of temperature change and to obtain knowledge of the pressures required over a range of temperature for this

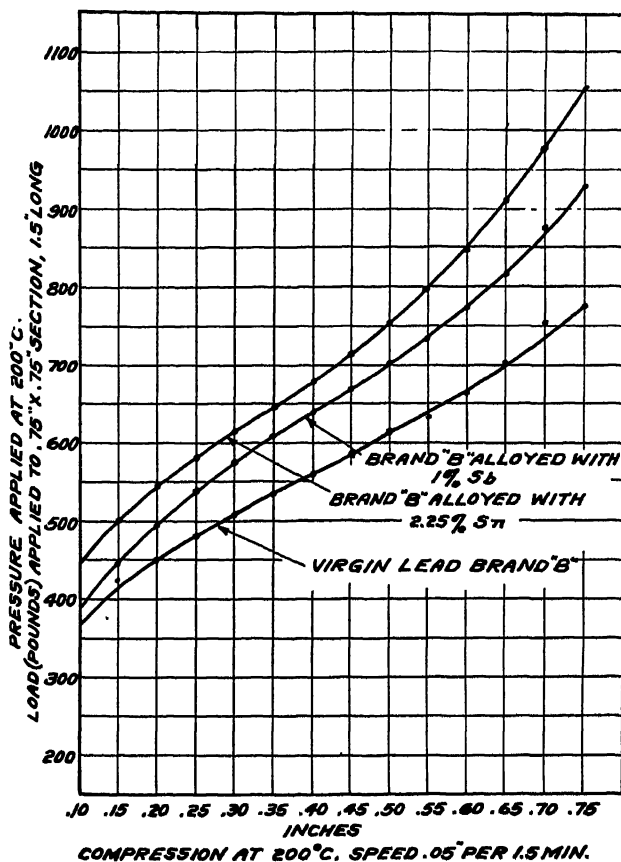


FIG. 9.—PRESSURES REQUIRED FOR VARIOUS ALLOYS OF BRAND B LEAD.

TABLE 8.—Results of Compression Tests on Group V—Brand D Lead

Deformation, In.	Load, Lb.				
	At 240° C.	At 220° C.	At 200° C.	At 180° C.	At 160° C.
0.15	160	190	230	275	370
0.25	175	210	250	295	405
0.35	190	230	275	325	440
0.45	215	255	300	370	470
0.55	240	290	340	415	520
0.65	275	330	385	465	580
0.75	320	380	455	535	665
TEMPERATURE, DEG. C.					
Start.....	240	221	202	180	160
Finish.....	241	220	201	180	160

particular type of test. The results are tabulated in Table 8, and plotted as curves in Fig. 11.

### SUMMARY

In lead cable-sheath extrusion different leads require different pressures. These compression tests on various brands of virgin pig lead and different alloys tested at 200° C. disclose the following:

When at a temperature of 200° C. the softest leads are those of highest purity, both copper-free and bismuth-free. Southeastern

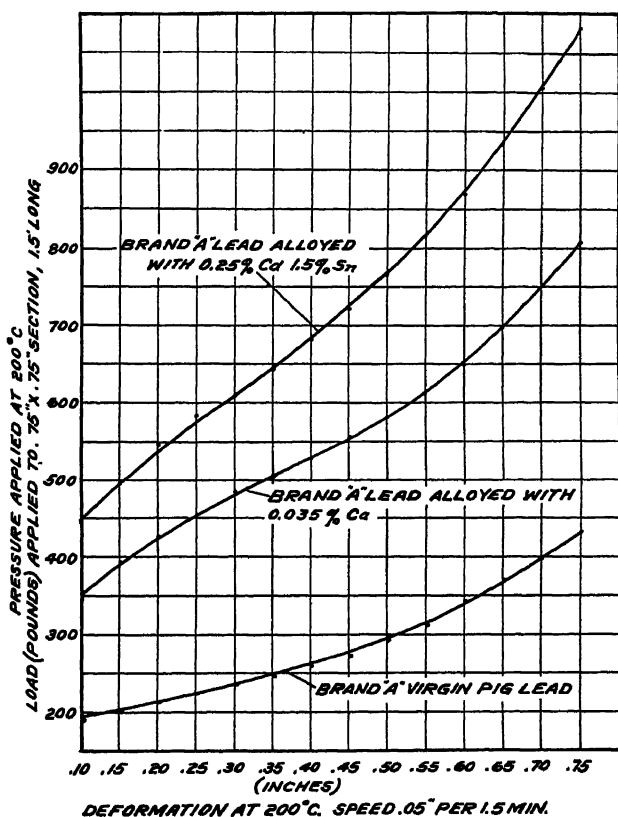


FIG. 10.—EFFECT OF CALCIUM AND CADMIUM TIN ON PRESSURE REQUIRED FOR DEFORMATION OF BRAND A LEAD AT 200° C.

Missouri lead, not desilverized and containing copper, requires a greater deformation pressure than a desilverized bismuth lead. See Fig. 2.

Copper alloyed with high-purity lead causes a rapid increase in deformation pressure up to 0.08 per cent copper. Copper present in larger amounts does not appreciably increase the deformation pressure. See Figs. 3, 4 and 5.

Bismuth alloyed with high-purity lead causes a gradual increase in deformation pressure. See Figs. 6 and 7.

Tin and antimony increase the deformation pressure of either a high-purity lead or a copper-bearing lead to about the same value. See Figs. 8 and 9.

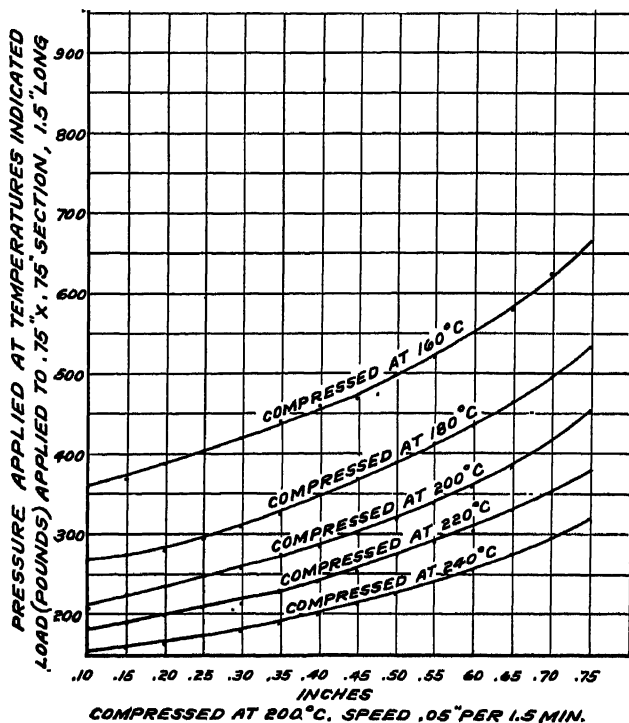


FIG. 11.—COMPRESSION TESTS AT DIFFERENT TEMPERATURES ON SPECIMENS PREPARED FROM BRAND D LEAD.

A very small amount of calcium appreciably increases the deformation pressure of a high-purity lead. See Fig. 10.

The effect of a variation in temperature from the 200° C. used in the tests described above is shown for one type of lead in Fig. 11.

## Effect of Temperature upon the Charpy Impact Strength of Die-casting Alloys\*

BY BERT E. SANDELL,† CHICAGO, ILL.

(New York Meeting, February, 1932)

MUCH has been said and written about the various uses of die castings, their applications in the various industries and their advantages and disadvantages. Examination of this literature, however, fails to disclose any data concerning the effect of temperature upon any of the physical properties of die-casting alloys.

The uses and applications of die castings are so numerous, and of such a varied nature, that far too lengthy a manuscript would be required to list all of them. Brief mention of some specific cases will suffice to illustrate the temperature ranges in which certain die castings function. Automobile hardware, such as hub caps, door handles, radiator caps, etc., can be used as one example. Castings of this type are constantly exposed to varying climatic conditions, temperatures ranging from below zero to upwards of 100° F. Refrigerator parts, such as ice-cube trays, etc., form another example. Approaching the other temperature extreme, we encounter conditions such as are found in kitchens in which oven-heat indicator parts, cooking utensils, waffle grids, etc., embody use of die castings, where temperatures as high as 500° F. are often met with.

Because of this variation in service temperatures, it was felt necessary to ascertain the effect of these temperatures upon the physical properties of die-casting alloys. The Charpy impact test was chosen first because of its simplicity, and because of the fact that brittleness is more likely to be objectionable in die castings than hardness or other physical properties.

### ALLOYS INVESTIGATED

Two types of alloys were used in this investigation—zinc-base and aluminum-base alloys. Two alloys of each group were included. Those most generally employed in the industry at present were selected.

Alloys A and B are of the same nominal composition, and correspond to A. S. T. M. alloy XXI, containing 4 per cent aluminum, 3 per cent copper, 0.1 per cent magnesium, and the balance zinc of 99.99 per cent

\* This paper won the second prize, Chicago Section Award, A. I. M. E. Presented before Chicago Section, March, 1931.

† Assistant Metallurgist, Stewart Die Casting Corporation.

purity. It should, however, be pointed out that alloy A was cast almost two years later than alloy B, and that the magnesium and copper contents of B are higher than those of A. These points, together with the fact that an improved technique was employed when alloy A was cast, explain the great difference between their impact strengths at room temperature. The impact strength of alloy B, as recorded in Table 4, therefore, is not indicative of what can be expected of the zinc-base alloys being used at the present time.

Alloys C and D, of the aluminum group, are straight silicon-aluminum alloys, and correspond to A. S. T. M. alloys IV and V, respectively. Alloy C is identical with that used by A. S. T. M. Committee B-6 in its program, while alloy D differs from the Committee's No. V alloy in that the silicon is 1 per cent lower. Analyses of the four alloys are given in Table 1.

TABLE 1.—*Analyses of Specimens*

Alloy	Composition, Per Cent											Date Cast
	Cu	Si	Fe	Zn	Ni	Mn	Mg	Sn	Pb	Al	Cd	
A.....	2.10			Bal.			0.08	0.002	0.008	4.09	0.003	10/27/30
B.....	2.91			Bal.			0.11	0.002	0.004	3.88	0.003	12/12/28
C.....	0.24	5.11	1.89	0.11	0.22	0.04	0.01			Bal.		3/4/27
D.....	0.12	11.58	1.25	0.28	T	0.08	0.03	T	none	Bal.		8/23/30

### TESTING PROCEDURE

An Amsler Charpy impact machine of 12 ft.-lb. capacity was used throughout the test, with one exception. An Amsler Charpy machine having a capacity of 15 ft.-lb. was used when determining the impact strength of alloy A at the room temperature. No machine of higher capacity was available for testing alloy A at the higher temperatures. A 40-mm. span was used with the specimens 3 in. long.

Five bars of each alloy for each temperature were selected. These were standard A. S. T. M. impact bars,  $\frac{1}{4}$  in. square and 6 in. long, each one cut in half. The impact strength at each temperature, therefore, is the mean of 10 determinations.

Six temperatures were used in the test: 0°, 32°, 70°, 212°, 350°, and 500° F. The 0° F. temperature was obtained with a mixture of snow and CaCl<sub>2</sub>. The 32° point was maintained in a vessel containing finely chipped ice in water. Room temperature sufficed for the 70° point, while boiling water served for that of 212°. A bath of tempering oil composed of 75 per cent tallow and 25 per cent steam cylinder oil was used in maintaining the 350° temperature. To obtain 500°, a tempering salt composed of equal parts of NaNO<sub>2</sub> and NaNO<sub>3</sub> was employed in the molten state. The accuracy of control is shown in Table 2.



TABLE 2.—Control of Temperature

Temperature, Deg F.	Medium Used	Outside Control	Accuracy of Temperature Control
0	Snow and $\text{CaCl}_2$	Snow pack	$-2^\circ$ to $6^\circ$
32	Chipped ice— $\text{H}_2\text{O}$	Snow pack	Exactly $32^\circ$
70	Room		
212	Boiling water	Electric hot plate	Exactly $210^\circ$
350	Tempering oil	Electric hot plate	$345^\circ$ to $360^\circ$
500	Fused $\text{NaNO}_2\cdot\text{NaNO}_3$	Bunsen flame	$435^\circ$ to $515^\circ$

For the lower temperatures the bars were placed loosely in a beaker filled with freezing mixture, and this beaker was placed within a larger beaker also containing the freezing mixture. With the higher temperatures the bars were stacked on trays so that all the surfaces came in contact with the temperature medium. About two hours were allowed for the bars to acquire the desired temperature. The tests at each temperature were run on the four alloys at the same time.

The bars were handled with tongs at the temperature of the medium, the exact position of the bars on the machine being pre-determined before removing from the temperature medium. The time interval between the medium and the impact was found to be 3 seconds.

## RESULTS AND CONCLUSIONS

The results are indicated in Table 3 and plotted in Fig. 1.

The following conclusions are believed justified from the data submitted.

1. The impact strength of this die-cast zinc-base alloy varies with temperature. The alloy is brittle at low temperatures and toughens as the temperature rises, reaching a maximum somewhere below the critical temperature of decomposition of the beta phase.

2. Two die-cast aluminum-silicon alloys exhibit no appreciable variation in impact strength from  $0^\circ$  to  $500^\circ\text{F}$ .

It is realized that the data submitted here are the results of an investigation quite preliminary in nature. More work remains to be done not only with these alloys but with others that are in greater use today. The information submitted, however, has not heretofore been presented,

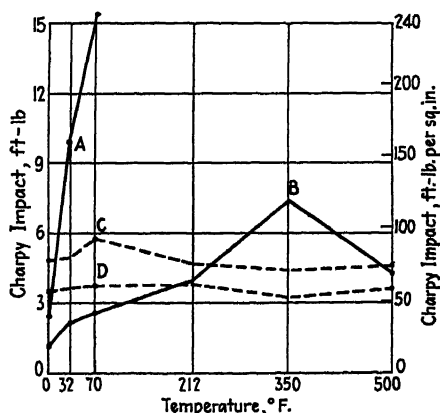


FIG. 1.—SUMMARY OF RESULTS, AS OUTLINED IN TABLE 3.

Each point on the curves represents the mean of 10 individual determinations.

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and it is believed that it will be valuable to the engineer considering the use of die castings.

TABLE 3.—*Summary of Results*

Points on Fig 1	0° F.	32° F.	70° F.	212° F.	350° F.	500° F.	
A Actual Charpy impact.... Ft-lb per sq. in.....	2.44 39.04	9.91 158.56	15.70 251.20				A. S. T. M. XXI
B Actual Charpy impact.. Ft-lb. per sq. in .....	1.14 18.24	2.09 33.44	2.60 41.60	4.02 64.32	7.44 119.04	4.25 68.64	A. S. T. M. XXI
C Actual Charpy impact. . Ft-lb. per sq. in....	4.80 76.80	4.94 79.04	5.73 91.68	4.67 74.72	4.41 70.56	4.63 74.08	A. S. T. M. IV
D Actual Charpy impact ... Ft-lb per sq. in.....	3.50 56.00	3.69 59.04	3.76 60.16	3.85 61.60	3.24 51.84	3.60 57.60	A. S. T. M. V

## The Role of the Platinum Metals in Dental Alloys

BY E. M. WISE,\* BAYONNE, N. J., WALTER S. CROWELL,† PHILADELPHIA, PA. AND  
J. T. EASH,‡ BAYONNE, N. J.

(New York Meeting, February, 1932)

THE practice of dentistry, particularly the construction of artificial dentures and "bridges," involves a unique and difficult application of the precious-metal alloys. Appliances used in the mouth are continuously exposed to corrosive agencies which can hardly be described as mild, and must remain free from tarnish and be substantially immune to corrosion. Limitations with respect to space and weight demand high physical properties, while complexity of form requires ease of working. The high corrosion resistance required necessitates the use of alloys of high precious metal content. The usual expedient of resorting to mechanical working to produce the requisite strength and stiffness cannot be utilized because of the frequency of annealing and soldering operations.

To meet these difficult conditions manufacturers of dental goods were early led, unknowingly perhaps, to the production of precipitation-hardening or temperable alloys.

The excellent properties of iridium-platinum may have suggested the addition of platinum metals to the conventional gold-silver-copper alloys to produce greater strength and hardness. It was found that such quaternary alloys retained their high physical properties after passing through the usual soldering process; *i. e.*, heating to 750° to 800° C. and cooling naturally in the air. Later it was discovered that they could be softened and rendered more ductile by heating to the same temperature and quenching in water. These early examples of precipitation hardening, for years the common knowledge of dental practitioners and laboratory technicians, escaped the attention of the scientific world and discovery of the transformation which was responsible for this hardening was disclosed by the Russian investigators of the system Au-Cu, Kurnakow, Schemtschushny and Zasedatelev,<sup>(1)</sup> although the optimum conditions for securing good properties in aged alloys were not given attention.

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† Technical Assistant to Vice-President, S. S. White Dental Mfg. Co.

‡ Metallurgist, Research Laboratory, International Nickel Co.

§ Superior figures in parentheses refer to list of references at end of paper.

It is now known that while certain of the gold-silver-copper alloys age-harden,<sup>(2)</sup> these ternary alloys do not respond as satisfactorily to heat treatment as do the quarternary alloys containing the platinum metals. Above 18 kt. (75 weight per cent) gold content, the ternary gold-silver-copper alloys with the usual silver to copper ratios do not effectively respond to heat treatment. The really strong gold-silver-copper alloys lie in the 12 to 16-kt. region but these alloys are deficient in corrosion resistance. These platinum-free low-carat alloys melt in the neighborhood of 850° C., making successful soldering uncertain; however, tensile strength approaching 100,000 lb. per sq. in. and elongations of 10 per cent or more can be obtained, in wrought alloys of this type. A wide range of jewelry alloys are responsive to precipitation hardening, as noted by Wise.<sup>(3)</sup> Alloys containing platinum metals can be made with 75 wt. per cent or more of the noble metals, gold, platinum and palladium, possessing ample corrosion resistance, melting points higher than 950° C., and tensile strengths of 150,000 to 170,000 lb. per sq. in., coupled with elongations of 10 per cent. These alloys are very responsive to simple heat treatments and are particularly suitable for dental uses.

Not many years ago the effect of the platinum metals in lightening the color of these high-strength ductile dental alloys was considered an unfortunate accompaniment of the improvement in physical properties occasioned by their presence. Recently the popularity of platinum and white gold jewelry, and the realization that a silver or a platinum white metal was less conspicuous than yellow gold, when placed against the teeth, has led to the more liberal use of the platinum metals in an effort to produce substantially "white" alloys.

The development of high-strength alloys was at first altogether empirical, the amount and the particular platinum group metal used being influenced by the relative market price of the several platinum group metals. This resulted in the production of what appeared to be extremely complex alloys frequently containing five, and in a few cases as many as eight, metallic elements. When studied from the standpoint of atomic percentage composition rather than weight percentage, and with an appreciation of the mutual equivalence of certain of the elements with respect to their ability to induce age-hardening, much of the complexity vanishes and the similarity between the various alloys in use, rather than their difference, becomes the striking feature.

The essential constituents of these alloys are platinum, palladium, gold, silver and copper. Zinc is added chiefly as a deoxidizer and promoter of soundness but in addition has a considerable hardening action. Alloys free from gold but containing one of the platinum metals in its stead likewise develop excellent properties, and will be briefly touched upon in subsequent sections.

In studying the general properties of polynary alloys, it is convenient and profitable to consider the atomic percentages rather than the weight percentages of the elements present. To facilitate this, all of the diagrams presented herewith have been prepared on the atomic per cent basis and summarize much of the reasonably credible information available on pertinent alloys. In preparing these diagrams currently accepted values for the melting points and, in certain cases, data with respect to other properties of the pure metals have been employed, which may differ to some extent from those given by the original investigators. It is felt that this course is justified and that it will tend to increase the utility of the diagrams presented.

The primary objects of the present paper are to summarize the existing information on the binary systems of particular importance in considering the higher order systems used in dentistry and to present new data upon the result of replacing various amounts of gold by platinum or palladium, thus affording some insight into the quaternary systems of interest for dental and other purposes.

The properties of the pure metals involved are sufficiently well known so that no extensive discussion of them will be made. The binary systems are less well known and recent work has led to a considerable amplification of our knowledge of them, so that it is thought desirable to summarize this information on a common basis. This summary, which constitutes Section I, comprises the binary systems Ag-Cu, Au-Ag, Au-Cu, Pd-Au, Pd-Ag, Pd-Cu, Pt-Au, Pt-Ag, Pt-Cu, and the ternary systems Au-Ag-Cu and Pd-Ag-Cu.

The mechanical properties of two parallel series of quaternary alloys—those of the systems Pt-Au-Ag-Cu and Pd-Au-Ag-Cu—are presented in Section II. The tensile properties of these alloys, after a variety of thermal treatments, are summarized and the remarkable improvement in the properties of the gold-base alloys occasioned by the replacement of a portion of the gold by platinum or palladium is demonstrated.

## SECTION I.—BINARY AND TERNARY SYSTEMS

BY E. M. WISE AND WALTER S. CROWELL

### *Silver-copper*

The system silver-copper was one of the earliest systems investigated by thermal methods, and it is indeed a tribute to the work of Heycock and Neville<sup>(5)</sup> to note how slight have been the corrections to their determination of liquidus and solidus temperatures resulting from recent work. The system is a simple eutectiferous one, the eutectic composition being 60.2 at. per cent Ag, 39.8 at. per cent Cu (71.94 wt. per cent Ag, 28.06 wt. per cent Cu)<sup>(6)</sup> and the eutectic temperature 779.4° C.<sup>(7)</sup>

The solubility of copper in silver has been carefully studied by D. Stockdale<sup>(8)</sup> and others, while the influence of annealing and precipitation-hardening treatments upon the mechanical properties of the silver-rich alloys has also received much attention, notably by Norbury,<sup>(9)</sup> Leach and Chatfield,<sup>(10)</sup> Wise,<sup>(11)</sup> Nowack,<sup>(12)</sup> Fraenkel and Nowack,<sup>(13)</sup> and others. The probable maximum values of strength and hardness attainable by aging are indicated in Fig. 2.

The copper-rich alloys also have been studied by a number of investigators. The closely agreeing results of Stockdale<sup>(8)</sup> and C. S. Smith<sup>(14)</sup>

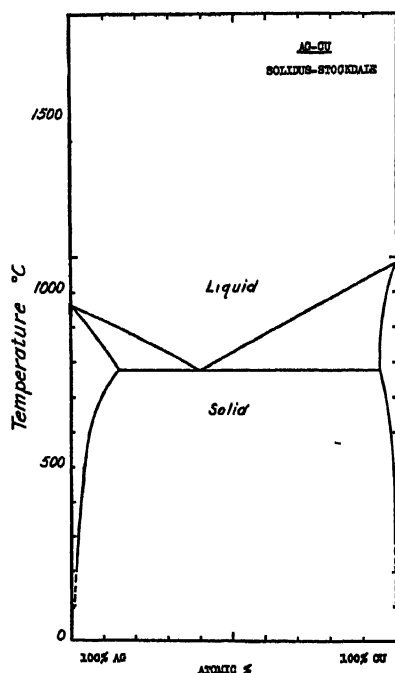


FIG. 1.

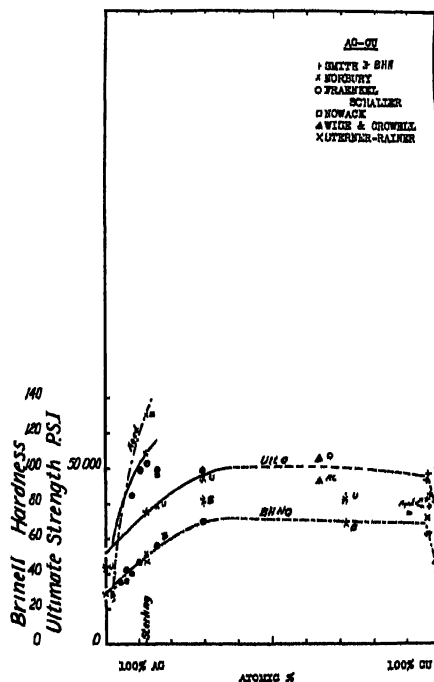


FIG. 2.

with respect to the solubility of silver in copper have been used in Fig. 1. Smith<sup>(14)</sup> investigated the possibilities of hardening these alloys by the precipitation of the silver-rich solid solution and found that while some hardening could be secured in this manner, the tensile strength was not increased, but in most cases was actually reduced by such treatments.

The maximum solubility of copper in silver at the eutectic temperature is 14.3 at. per cent, while that of silver in copper is 5 at. per cent. The minimum solubilities are about 1.5 at. per cent Cu and 0.2 at. per cent Ag, or less, respectively, as indicated in Fig. 1.

The melting points of these alloys are low, but they do show a marked tendency to absorb oxygen, so that appropriate means for reducing this absorption and for removing it prior to casting are essential. The sterling silver alloys are frequently deoxidized by the addition of a small amount of phosphorus just prior to pouring. This is quite effective and does not impair the surface of the resulting ingot as many other deoxidizers are apt to do. The absorption of sulfur during melting should also be guarded against.

The rolling and general fabrication of these alloys is very simple. In annealing, a steam or other more or less neutral atmosphere is helpful and its use avoids the necessity for extensive pickling to remove the cuprous oxide which otherwise would form.

Both the silver-rich and copper-rich solid solutions are soft and ductile, so that the mechanical properties of the binary alloys are quite orthodox. Due to the change in the mutual solubility the tendency is for the tensile strength of the duplex alloys to be slightly increased as the quenching temperature is raised.

The color of the copper-rich phase is pink, while that of the silver-rich phase is almost as white as pure silver. The colors of the intermediate alloys, consisting as they do of mixtures of the above phases, are practically a linear function of the amounts of the two phases present.

The corrosion resistance of the silver-rich alloys is only moderately good and becomes worse when appreciable quantities of the copper-rich phase are present. The resistance of these alloys to atmospheric tarnishing is poor, owing to the rather rapid formation of silver sulfide.

### *Gold-silver*

The system gold-silver comprises a continuous series of solid solutions with a liquidus and solidus intermediate between the melting points of the component pure metals. The solidus is close to the liquidus throughout the series, as shown in Fig. 3, which is based on the results of Sterner-Rainer.<sup>(15)</sup>

The solid solutions formed are all soft and ductile and the tensile strengths of the annealed alloys reach a maximum of 28,500 lb. per sq. in. at 50 at. per cent (64.6 wt. per cent) Au, as indicated in Fig. 4, computed from Sterner-Rainer's<sup>(15)</sup> results.

Melting the gold-rich alloys is a pleasure and gives virtually no trouble. The alloys containing considerable silver show some tendency to "spit" on cooling if melted under oxidizing conditions. Aside from this the alloys are very simple to handle, and because of their softness and high ductility their fabrication occasions very little trouble.

The corrosion resistance increases more or less steadily with the gold content, as does the resistance to tarnishing. Alloys containing 50 to

60 at. per cent Au (64.6 to 73.3 wt. per cent) or 15.5 to 17.5 kt., are quite resistant to tarnishing in the atmosphere and to oral corrosion.

The addition of silver to gold gradually lightens the yellow color characteristic of gold but the color passes through a distinct greenish shade in the vicinity of 57.2 to 62.1 at. per cent Au (71 to 75 wt. per cent), or 17 to 18 kt. Further additions of silver result in the production of slightly greenish whites at 35.4 at. per cent Au (50 wt. per cent) or 12 kt. These alloys tarnish, however, and for this reason are unsuitable for general use.

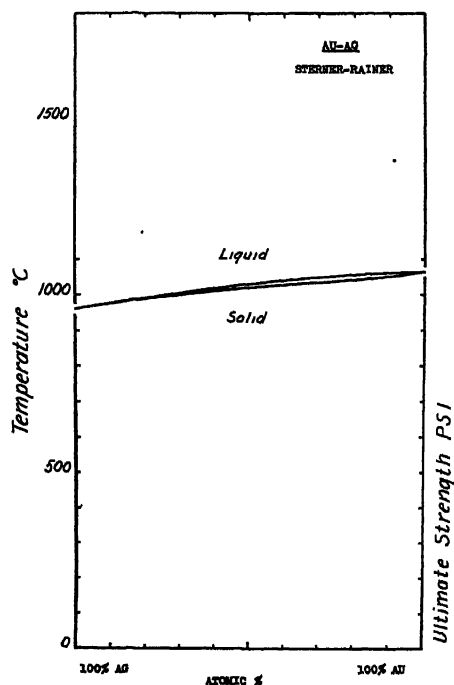


FIG. 3.

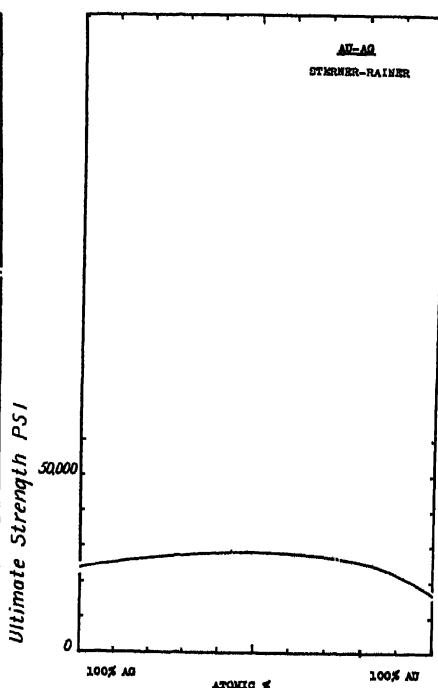


FIG. 4.

### Gold-copper

The system gold-copper comprises a continuous series of solid solutions stable above about 450° C. The liquidus and solidus are close together throughout and pass through a minimum of 885° and 883° C. respectively at 50 at. per cent (75.6 wt. per cent) Au, as noted in Fig. 5, based on Sterner-Rainer's results.<sup>(15)</sup>

Solid-solid transformations occur in this system leading to the formation of the compounds approximating Au-Cu and Au-Cu<sub>3</sub>, as was first established by Kurnakow, Schemtschushny and Zasedatelev in 1916.<sup>(1)</sup> These transformations have been the object of much investigation in the past few years. Both of these compounds show considerable solubility



for copper and gold, and in consequence exist over a considerable composition domain. The compound Au-Cu is soft—differing in this respect from the more common types of intermetallic compounds—but by arresting its formation at the proper point marked precipitation hardening can be secured in spite of this. The compound Au-Cu and the related platinum metal-copper compounds are therefore of fundamental importance in the production of high-strength precipitation-hardening dental alloys. The compound Au-Cu<sub>2</sub> and its analogues are not of

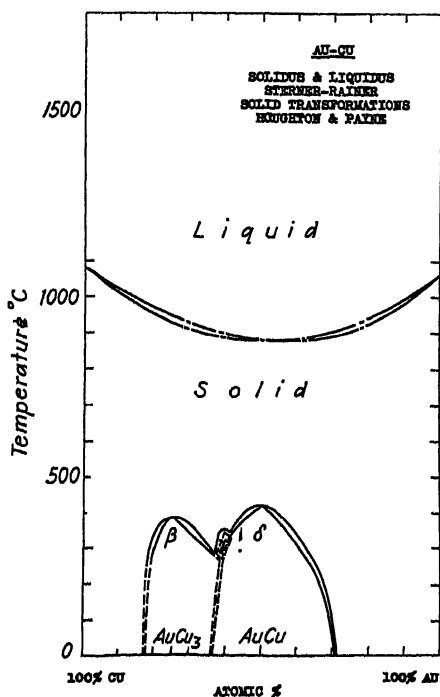


FIG. 5.

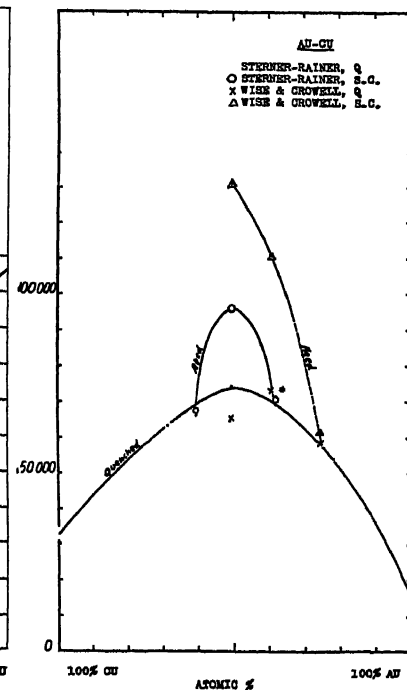


FIG. 6.

particular value, from the standpoint of dental alloys, because of the lack of nobility of alloys containing this phase.

The solid-solid transformations occurring in this system have been further studied by Kurnakow and Ageev<sup>(16)</sup> and by Haughton and Payne.<sup>(17)</sup> The results of these two investigations agree reasonably well except for slight differences in the maximum temperature of existence of the solid phases. The solid-solid transformations indicated in Fig. 5 are based upon the findings of Haughton and Payne; the maximum limit of the phase Au-Cu is indicated as being about 71 atomic per cent, as suggested by them. It seems probable, however, that at low temperatures the limit may extend to about 75 atomic per cent.

The tensile strength of the binary gold-copper alloys, annealed at about 700° C. and quenched, reaches a maximum of 74,000 lb. per sq. in. at 50 at. per cent (75.6 wt. per cent) Au, while that of the aged alloys likewise appears to reach a maximum at the same composition; but such aged alloys are characterized by very low elongations. The tensile data are summarized in Fig. 6, and are based on data by the authors and upon the results of L. Sterner-Rainer.<sup>(15)</sup>

The melting of the alloys offers little difficulty, except that due to the oxidation of the copper, which can be avoided by appropriate

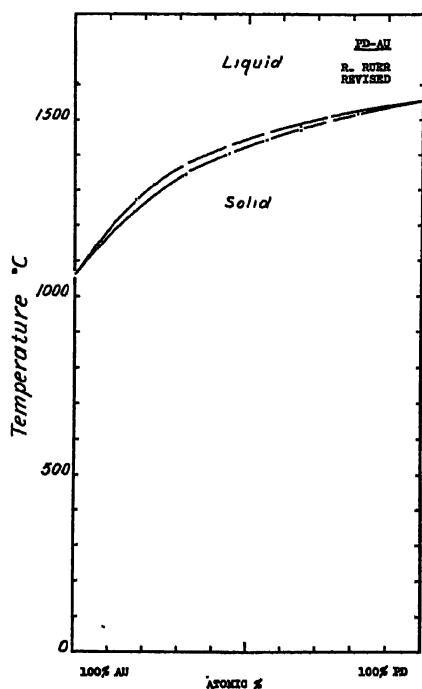


Fig. 7.

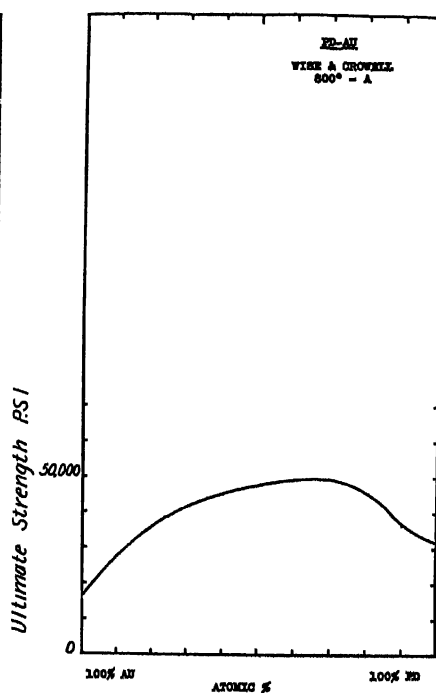


Fig. 8.

means. In general, the alloys are readily workable, although those in the vicinity of 50 at. per cent (75.6 wt. per cent) Au are troublesome because of the formation of the phase Au-Cu. Quenching alloys approximating this composition tends to preserve the solid solution, and thus to some extent improves their working properties.

The corrosion and tarnish resistance of these alloys is reasonably satisfactory as long as they contain not less than about 50 at. per cent (75.6 wt. per cent) or 18 kt. Au. The alloys containing smaller quantities of gold tarnish at a moderate rate, but this has not precluded their use for jewelry and other nondental purposes.

The addition of copper to gold darkens the yellow-gold color and leads to a definitely red color at 50 at. per cent (75.6 wt. per cent) or 18 kt. Au. This red color persists to the copper end of the series.

### *Palladium-gold*

The system palladium-gold consists of a continuous series of solid solutions quite free from solid-solid transformations. The liquidus rises very rapidly at the gold end and then more slowly as the palladium end is approached. The solidus is close to the liquidus throughout, and for this reason little difficulty from liquation is experienced. The equilibrium diagram is given in Fig. 7, slightly modified from that reported by R. Ruer.<sup>(18)</sup>

The alloys are all reasonably soft and are very ductile. The tensile strength of the alloys annealed at 800° C. reaches a maximum of 49,500 lb. per sq. in. at 65 at. per cent Pd as shown in Fig. 8. These results were obtained by one of the authors on alloys prepared by F. E. Carter.

The melting of the palladium-gold alloys offers no great difficulty if means are available for securing the requisite temperature and a reasonably high melting rate. The high-palladium alloys tend to pick up oxygen when molten and evolve it during cooling, an effect which can be minimized by the use of a reducing atmosphere toward the end of the melting period.

The tarnish resistance of these alloys is excellent and the alloys containing above 12 at. per cent (20 wt. per cent) Au are resistant to nitric acid. The high melting point of most of these alloys and their corrosion resistance has led to their use in the form of laboratory ware and rayon spinnerets.

The addition of palladium to gold rapidly masks the yellow color of the latter metal, so that alloys containing 24.8 at. per cent (15 wt. per cent) and upward of palladium are quite white.

### *Palladium-silver*

This system closely resembles that of palladium-gold and consists of an uninterrupted series of solid solutions apparently free from transformations in the solid state. The liquidus rises rapidly upon the addition of small quantities of palladium and then rises slowly as the palladium end is approached. The solidus is close to the liquidus throughout, although the spread appears to be slightly greater than in the palladium-gold system. The equilibrium diagram is given in Fig. 9 and is slightly modified from the results reported by R. Ruer.<sup>(19)</sup>

The alloys are all soft and extremely ductile. The tensile strength of alloys annealed at 800° C. attains a maximum of 59,500 lb. per sq. in. at 70 at. per cent (69.8 wt. per cent) Pd, as shown in Fig. 10, which is based on the results of one of the authors. These results are based on

tests made on alloys supplied by F. E. Carter. The Baby Brinell hardness of these alloys, as determined by F. E. Carter,<sup>(20)</sup> are shown in the same figure.

The melting of these alloys and the production of sound castings thereof is more difficult than it is with palladium-gold alloys, because of the propensity of the silver to absorb oxygen when molten and to evolve it during cooling. By the use of a sufficiently reducing atmosphere during the latter part of the melt—or better, by the addition of suitable

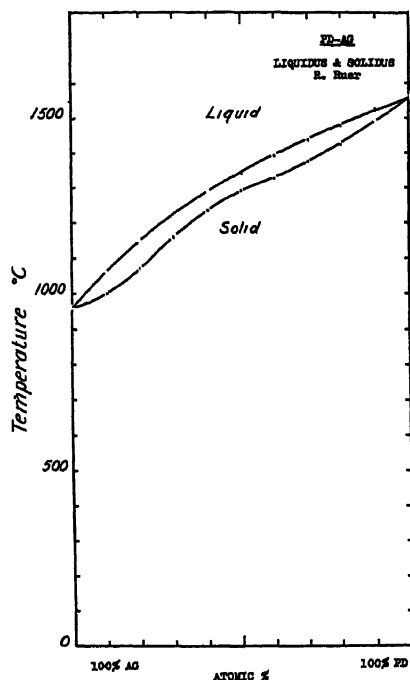


FIG. 9.

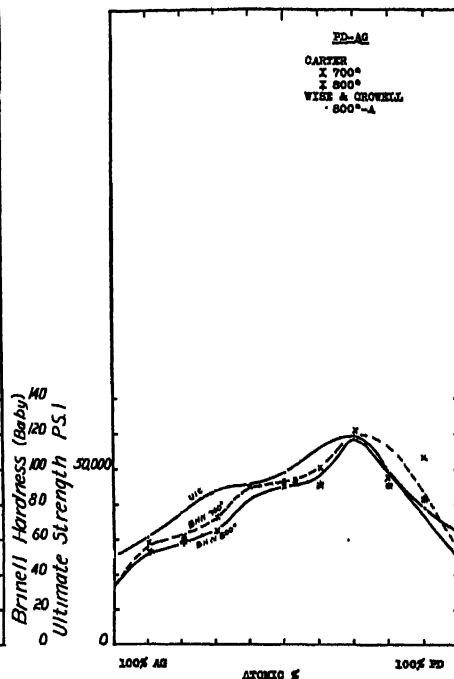


FIG. 10.

deoxidizers such as calcium boride—this difficulty can be surmounted and blister-free metal can be produced.

The addition of palladium to silver produces an improvement in tarnish resistance—rather slowly until about 25 at. per cent Pd is added, then more rapidly until about 40 at. per cent Pd is present, at which composition a very substantial resistance to tarnishing is evident. Further additions of palladium produce additional resistance to tarnishing such that alloys containing 50 to 55 at. per cent Pd and above may be regarded as being very resistant to atmospheric tarnish. The resistance to oral corrosion becomes satisfactory when the palladium content exceeds some 50 to 55 at. per cent.

All of the alloys are white, although the intermediate alloys are less brilliantly so than the end members.

### *Palladium-copper*

The system palladium-copper comprises a continuous series of solid solutions stable above about 670° C. The liquidus and solidus remain close together throughout the system. The available data are summarized in Fig. 11 and are slightly modified from the diagram presented by R. Ruer.<sup>(21)</sup>

Solid-solid transformations—much resembling those of the gold-copper alloys—occur at low temperatures and have been studied in detail by Sedstrom,<sup>(22)</sup> Holgersson and Sedstrom,<sup>(23)</sup> Johansson and Linde<sup>(24-25)</sup>, and by Borelius, Johansson and Linde.<sup>(26)</sup> These investigators have established the occurrence of phases based on Pd-Cu<sub>3</sub> and Pd-Cu. The former shows considerable solubility for copper and palladium, while the latter appears to be able to dissolve copper only, so that its composition domain terminates sharply at 50 at. per cent (62.6 wt. per cent) Pd. These compounds have been found by one of the present authors to afford a means for precipitation-hardening the binary palladium-copper alloys as well as the ternary alloys containing silver or other metals.

Borelius, Johansson and Linde found considerable hysteresis to occur in these transformations and proposed a double diagram based on the temperature of transformation during heating and cooling cycles. This proposal seems untenable and the curves shown in Fig. 11 are drawn to approximate the temperature at which the transformation occurred on heating. In this connection, it may be profitable to consider the work of Howard Scott<sup>(34)</sup> in connection with the influence of volume and resultant pressure changes upon the progress of transformations in the solid state.

The tensile strength of the quenched alloys (annealed for 5 min. at 700° or 750° C.) reaches a maximum of 93,000 lb. per sq. in. at 50 at. per cent (62.5 wt. per cent) Pd, while that of the aged alloys reaches a peak value of 116,000 lb. per sq. in. at 45 at. per cent (57.9 wt. per cent), as indicated in Fig. 12.

The (Baby) Brinell hardness of the palladium-copper alloys, hard-rolled and then annealed for 5 min. at 700° and 800° C., as determined by F. E. Carter,<sup>(37)</sup> is indicated in Fig. 12.

The melting and casting of these alloys is somewhat more difficult than similar operations with the analogous gold-copper alloys, because of their higher melting points and greater tendency to absorb oxygen, but the methods that were suggested in connection with the palladium-silver alloys are applicable, and good, sound ingots can be produced. The

working of the transformable alloys is a little troublesome because of the considerable hardness developed during processing, but is not serious.

The tarnish resistance of these alloys is perhaps slightly inferior to the palladium-silver alloys of the same atomic composition and all of the alloys of substantial tarnish resistance, and otherwise suitable for dental purposes, are quite white—the palladium serving to obliterate the copper color.

The color of the palladium-copper alloys ranges from red to substantially white upon the addition of less than 25 at. per cent Pd; alloys containing larger quantities of palladium are, of course, white.

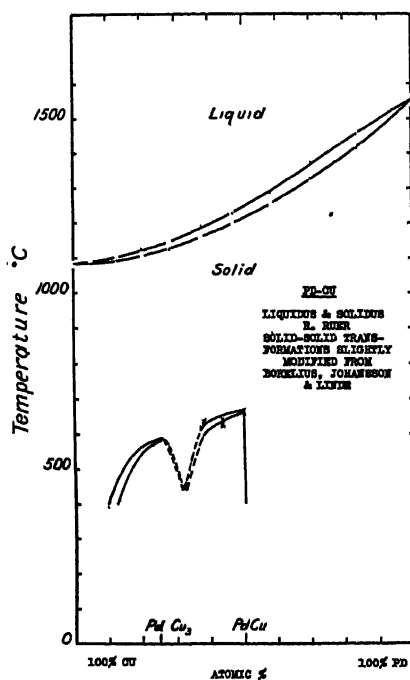


FIG. 11.

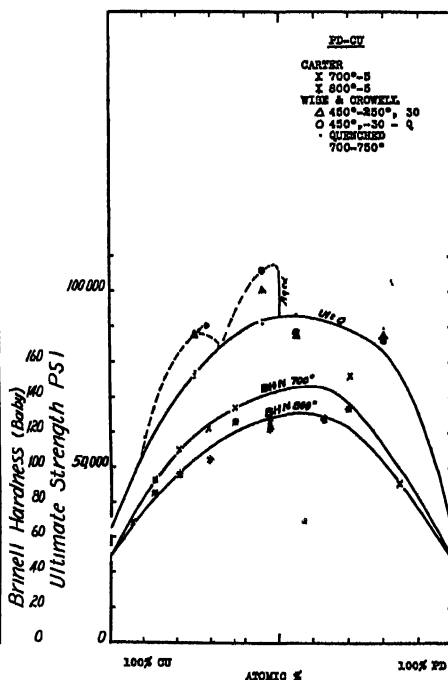


FIG. 12.

### Platinum-gold

This system for many years was regarded as being of the simple solid solution type notable for the great spread between the solidus and liquidus over most of its composition domain. Doerinckel<sup>(28)</sup> investigated this system in 1907 and his findings have been generally accepted, although Grigorjew<sup>(29)</sup> recently reported results in radical disagreement with this early work. Johansson and Linde's<sup>(30)</sup> recent work confirms the type of diagram proposed by Doerinckel, and in consequence Doerinckel's findings are employed in the diagram presented in Fig. 13.

The difficulty of working all but the alloys near either end of the series had been known for years but the reason for this was not recognized until recently, when the excellent work of Johansson and Linde,<sup>(30)</sup> noted above, demonstrated that although the alloys did actually consist of an unbroken series of solid solutions at temperatures extending a slight distance below the solidus, important transformations occurred over much of the composition domain at lower temperatures.

The solid-solid transformations are of considerable practical and theoretical importance. The first transformation occurring as the

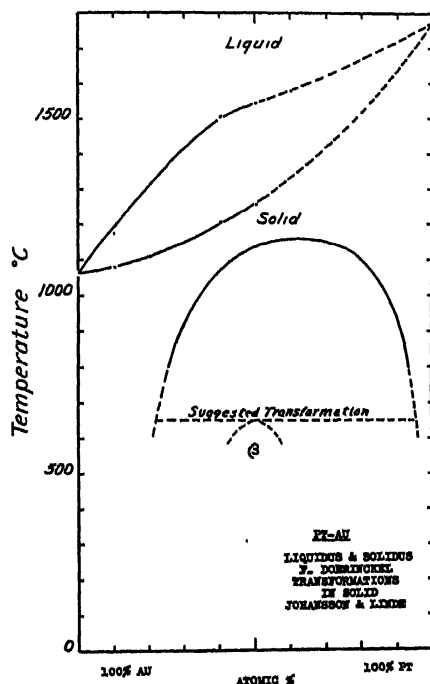


FIG. 13.

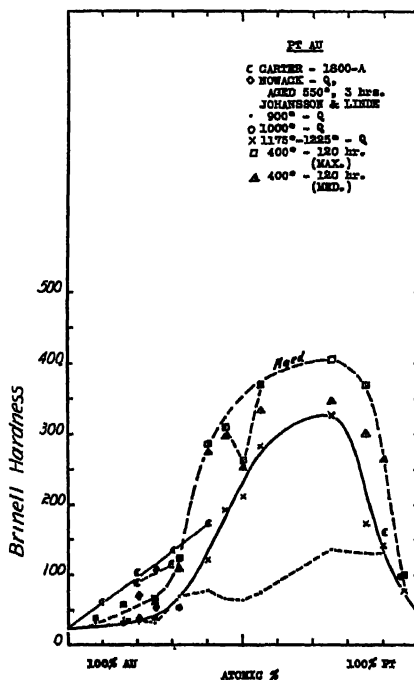


FIG. 14.

temperature is lowered below the domain of solid solution stability is the splitting of the solid solution into two components, one consisting of gold saturated with platinum and the other platinum saturated with gold. The compositions of the two phases change rather rapidly as the temperature falls. A further reaction occurs at about 650° C., leading, it is supposed, to the formation of the compound Au-Pt. That the two solid solutions could react to form such a compound is not impossible, but further work is required to definitely determine the nature of the phases stable at low temperatures. The solubility relations, as determined by Johansson and Linde, and the further transformation tentatively suggested by them, are indicated in Fig. 13.

That precipitation hardening could be obtained with the binary platinum-gold alloys was demonstrated some years ago in some unpublished work of one of the authors, and further work has been reported by Nowack<sup>(12)</sup> and Johansson and Linde.<sup>(30)</sup> The data of these workers regarding the hardness of the quenched alloys and various data from other sources concerning the hardness of the aged alloys are incorporated in Fig. 14.

The solubility of platinum in gold at temperatures in the vicinity of 400° to 500° C. is not well established but probably is about 12 at. per cent. The hardness composition diagram, as determined by Johansson and Linde, would indicate that the initial rate of increase in hardness of gold with the platinum content was very slight up to some 20 per cent Pt. This is not in accord with the results reported by Cartier,<sup>(27)</sup> and with more recent results which he has recently communicated to the authors.<sup>(20)</sup> The hardness composition diagram for the alloys aged at 400° C., as determined by Johansson and Linde, does not sharply intersect the hardness curve for the quenched alloys at the limit of solubility at the aging temperature, as it should if the alloys were initially homogeneous. It appears, therefore, that the quenched alloys used for hardness determinations were rather inhomogeneous. Severe coring, difficult to wholly efface, is known to occur in these alloys when they are prepared by fusion methods, as would be expected from the shape of the liquidus and solidus.

The alloys quenched from the homogeneous domain show a maximum hardness of 325 Brinell at 75 at. per cent platinum. It seems probable that this rather high value is in part due to some precipitation hardening occurring during the quenched cycle. Aging for some 120 hr. at 400° C. produces a further increase in hardness. Alloys so treated possess a maximum hardness of about 400 Brinell at 75 at. per cent platinum.

The melting of these alloys is not particularly difficult except for the difficulties occasioned by their high melting point, but the production of good castings of the intermediate alloys is a matter of extraordinary difficulty. This has been generally attributed to the tremendous spread between the liquidus and solidus over this region. The working of the gold-rich alloys down to some 70 at. per cent Au is not difficult if the initial ingot is sound. Working the platinum-rich alloys containing gold in quantities above about 5 at. per cent is difficult, as might be expected from the nature of the system.

The corrosion resistance of these alloys is exceptionally high and considerable use has been made of this characteristic in the construction of chemical plant equipment, particularly spinnerets for the production of rayon.

The color ranges from golden yellow through rather pale yellowish white at 30 at. per cent Pt. The alloys containing a platinum content



above this are rather white if quenched from a sufficiently high temperature, although the intermediate alloys are not very brilliant.

### Platinum-silver

The platinum-silver system consists of two series of solid solutions which coexist over the range 40 at. per cent (54.7 wt. per cent) Pt to 80 at. per cent (88 wt. per cent) Pt at the solidus temperature. The heterogeneous range is widened at lower temperatures, as is shown in Fig. 15, and is based on the results of Johansson and Linde.<sup>(31)</sup> The

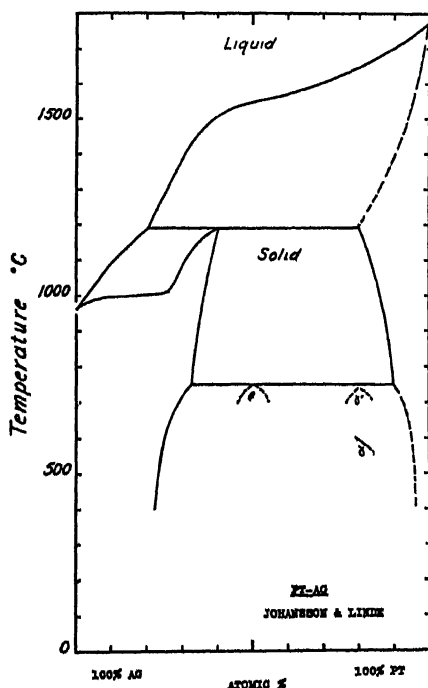


FIG. 15.

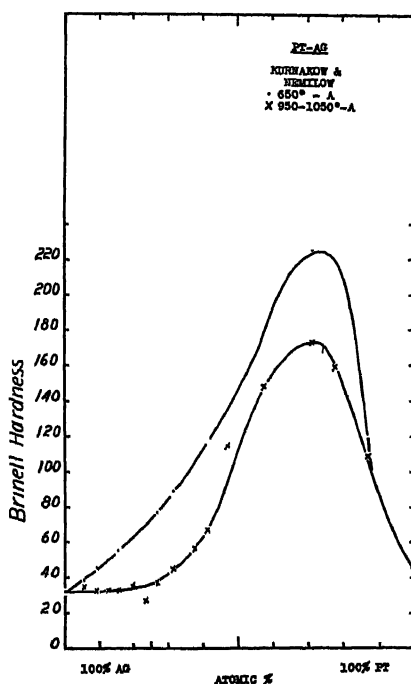


FIG. 16.

heterogeneous domain extends from about 23 to 96 at. per cent Pt at 500° C. Johansson and Linde further suggest that at low temperatures a phase approximately Pt-Ag may be formed, while a second phase containing some 80 at. per cent Pt may also be formed. The latter in turn suffers further transformation at lower temperatures. These reactions, as with platinum-gold, result in the formation of new phases from the interaction of two saturated solid solutions which show a considerable decrease in mutual solubility as the temperature falls.

The solid solubility of platinum in silver and silver in platinum decreases as the temperature falls, thus affording some possibilities for precipitation hardening, particularly if some copper is also present.

The Brinell hardness values of these binary alloys after annealing at 650° C. and at 950° to 1050° C., as determined by Kurnakow and Nemilow,<sup>(32)</sup> are shown in Fig. 16.

The extremely low rate of increase in the hardness of the silver-rich alloys, annealed at 950° to 1050° C., with an increase in platinum content is very peculiar and parallels certain results reported for the platinum-gold alloys. This may be due to the persistence of the cored structure developed during casting. The shape of the liquidus and the solidus is such that coring is very severe, and it is doubtless very persistent.

Melting and casting these alloys is rather difficult because of the propensity of silver to pick up oxygen and of the spread between the liquidus and solidus. Rolling sound alloys containing up to 40 at. per cent (54.7 wt. per cent) Pt is not unduly difficult, but the alloys containing larger proportions of platinum up to some 80 at. per cent (88 wt. per cent) are extremely difficult to work, and require quenching from a temperature of some 800° C. to make them even reasonably workable.

The corrosion and tarnish resistance of the silver-rich alloys increases with the platinum content, but from the nature of the system the rate of increase with the platinum content will be slower for platinum above 40 at. per cent until the platinum content reaches some 80 at. per cent. Above this point the nobility should rapidly approach that of pure platinum.

The colors of the alloys are substantially white throughout, although they are less brilliant than those of the component metals.

#### *Platinum-copper*

The system platinum-copper, like that of palladium-copper, comprises a continuous series of solid solutions stable at temperatures at and considerably below the solidus, as shown in Fig. 17. This diagram is slightly modified from the observations of F. Doerinckel.<sup>(28)</sup> Johansson and Linde<sup>(25)</sup> investigated this system and established the presence of the phases Pt-Cu<sub>3</sub> and Pt-Cu, both stable at low temperature and capable of dissolving appreciable quantities of copper and platinum, so that they exist over a considerable composition domain. The compound Pt-Cu is of particular interest in dental alloys as it is one of the important precipitable compounds responsible for the age-hardening observed in many commercial alloys. It is probably somewhat soluble in the phase Au-Cu, although the extent of this solubility is not accurately known.

Nowack<sup>(12)</sup> has observed that the formation of the phase Pt-Cu offers an effective means for hardening alloys in the vicinity of 50 at. per cent, while the results of one of the authors indicate that only very slight precipitation hardening occurs at 75 at. per cent Pt. The hardness composition relations are tentatively indicated in Fig. 17.

The melting and casting of the alloys of this series is a little troublesome because of the oxidizability of the copper and gas evolution on solidification but is not unduly difficult. The working of the intermediate transformable alloys is very difficult, as would be expected.

The compound Pt-Cu, according to Johansson and Linde's measurements of the electrical resistances of quenched and aged alloys, extends up to 82.5 at. per cent Pt. If the resistivities of the platinum-copper alloys, as reported by Carter,<sup>(27)</sup> were used in conjunction with Johansson and Linde's measurements on aged alloys, the phase limit would appear

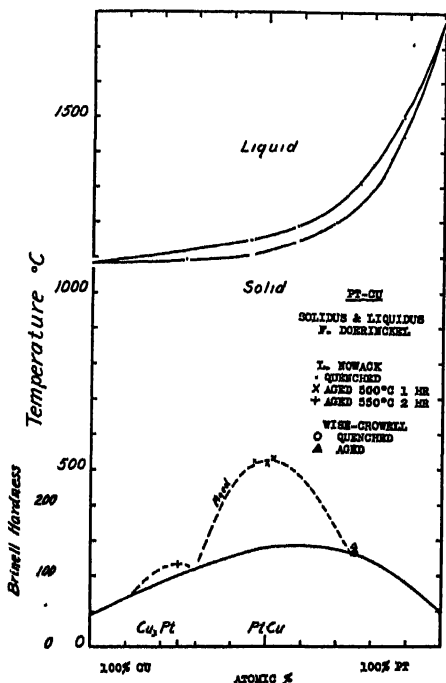


FIG. 17.

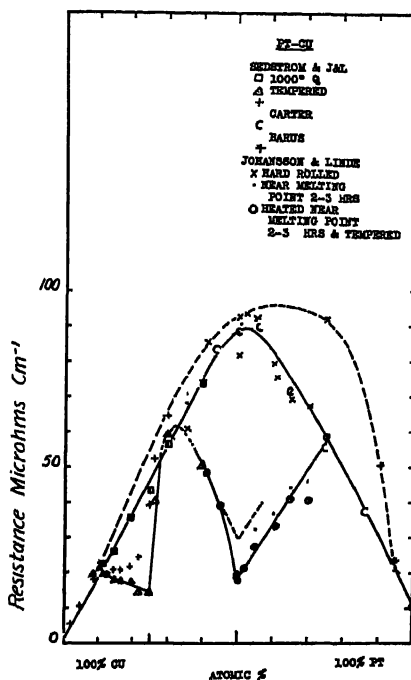


FIG. 18.

to extend to 75 at. per cent Pt, making it closely analogous to the system gold-copper.

The tabulated results of Johansson and Linde concerning the resistivities of aged alloys indicate a sharp minimum at 50 at. per cent and a more or less linear, steeply rising resistivity composition relation for alloys on either side of the equi-atomic point. From their results it appears that a small gap exists between the domain of the Pt-Cu<sub>3</sub> phase and the Pt-Cu phase. It is probable that a closer approach to equilibrium at low temperatures would eliminate this gap, as with the system gold-copper. The resistivity values on alloys of this system are summarized in Fig. 18.

*Gold-silver-copper*

The liquidus in this important system is characterized by a valley extending from the eutectic composition of the silver-copper system 779.4° C. at 39.8 at. per cent (28.06 wt. per cent) Cu, to the minimum of 885° C. in the gold-copper system, which is located at 50 at. per cent (24.4 wt. per cent) Cu. The solidus shows that the influence of the silver-copper eutectic is rather persistent, and consequently the solidus is rather

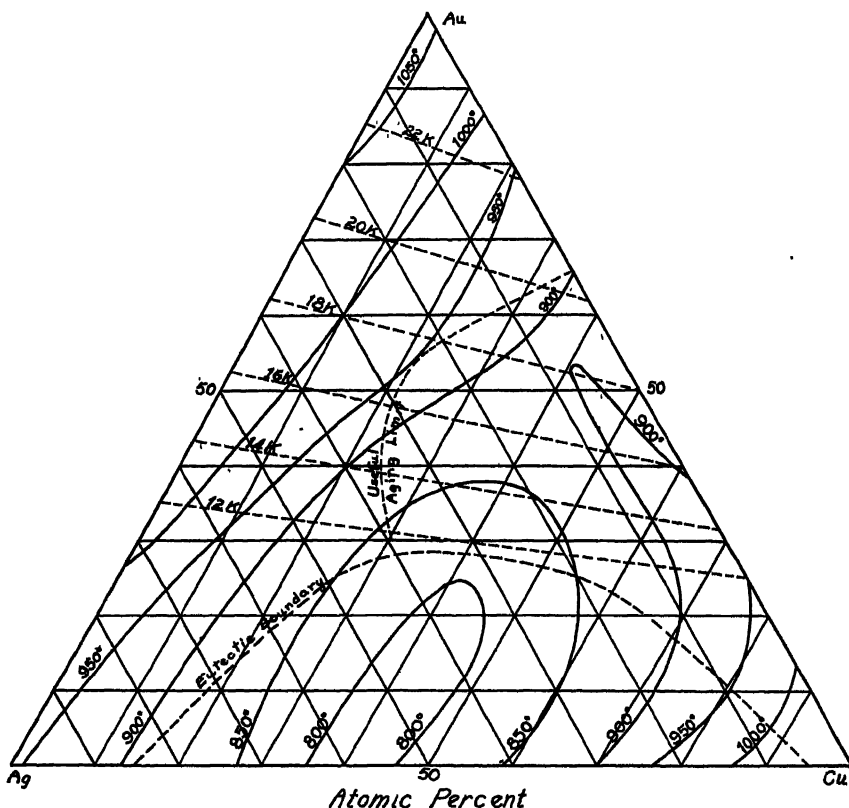


FIG. 19.—LIQUIDUS OF AU-AG-CU SYSTEM BASED ON STERNER-RAINER AND E. JANECKE.

low throughout much of the region near to and parallel to the silver-copper side. The liquidus is well represented in Fig. 19; it is based largely on the work of Sterner-Rainer<sup>(15)</sup> and Janecke.<sup>(33)</sup>

Solid-solid transformations, resulting in the production of new phases or a change in composition of pre-existing phases, occur between all of the components with the exception of the pair gold-silver, in consequence of which precipitation hardening is observed over a wide field. The approximate location of the gold-rich edge of the Au-Cu precipitation

field is indicated in Figs. 19 and 20. This curve delimits the region within which at least a 10 per cent increase in strength can be secured.

The tensile strengths of the quenched alloys are indicated in Fig. 20 and are based largely upon the work of Sterner-Rainer.<sup>(15)</sup> The portion of this diagram concerning the alloys with high gold content closely agrees with the work of one of the present authors.

The melting and casting of these alloys is not difficult in general and the previous remarks on the component binary systems involved apply

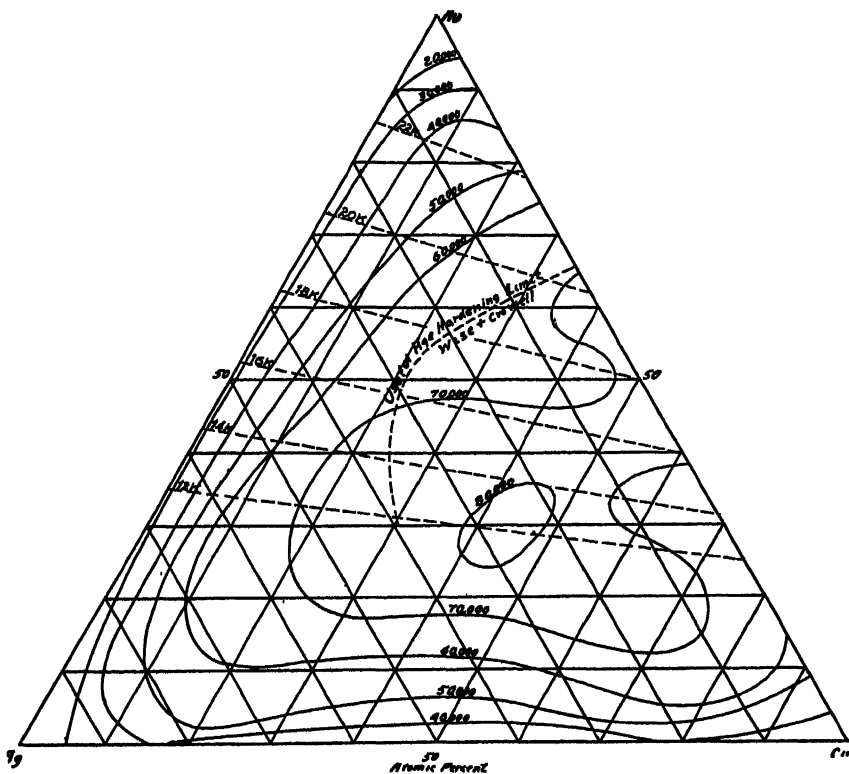


FIG. 20.—TENSILE STRENGTHS OF QUENCHED AU-AG-CU ALLOYS. COMPUTED LARGELY FROM STERNER-RAINER.

here with equal force. A small range of alloys extending from the red golds of 18 kt. to the reddish yellow 14-kt. alloys are rather hard and are somewhat prone to crack on rolling. Aside from this, their working properties are excellent.

The colors of the alloys range from yellow through a variety of shades of red, yellow, green and white. Only the yellow, green and red alloys are sufficiently tarnish resistant to be useful.

The corrosion resistance of the alloys is intermediate between that of the several binaries previously discussed.

*Palladium-silver-copper*

The liquids in this system rises rapidly as the palladium content is increased, and this characteristic is one of the important reasons for the use of palladium in dental alloys. The location of the solidus is not fully established but it certainly rises very rapidly upon the addition of palladium.

The solid-solid transformations of the binaries involved are evident in the ternary system, in consequence of which a wide domain of harden-

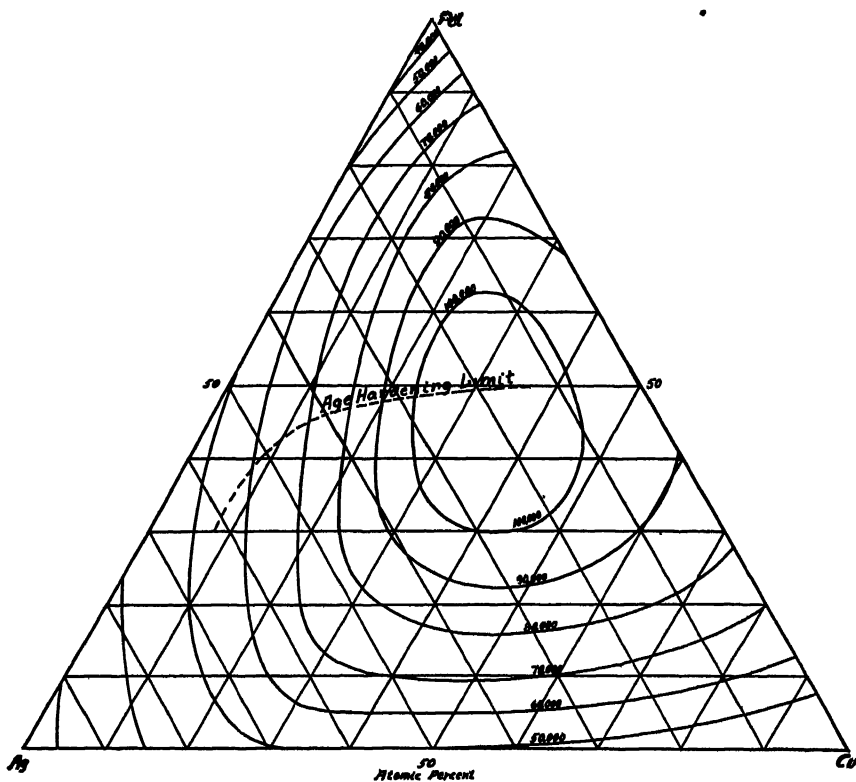


FIG. 21.—TENSILE STRENGTHS OF QUENCHED PD-AG-CU ALLOYS. (Wise and Crowell.)

able alloys has been found to exist by one of the present authors. The tensile strengths of the quenched alloys are summarized in Fig. 21, while the tensile strengths of certain of the ternary alloys, after quenching, and quenching and aging, are indicated in Fig. 22. In Fig. 21 the tensile strengths of Pd-Ag alloys annealed at 800° C. were employed, while the values for Pd-Cu and Pd-Ag-Cu alloys were based on results obtained after short anneals at 700° to 750° C., as is appropriate for high-strength dental alloys.

The melting of these alloys is complicated by troubles due to oxygen pick-up when molten and to its evolution during solidification, but this can be overcome by appropriate means. The working of the alloys is surprisingly easy in spite of the high strengths which can be secured by suitable age-hardening treatments.

The corrosion and tarnish resistance of these alloys, like those of the gold-silver-copper alloys, is intermediate between those of binaries

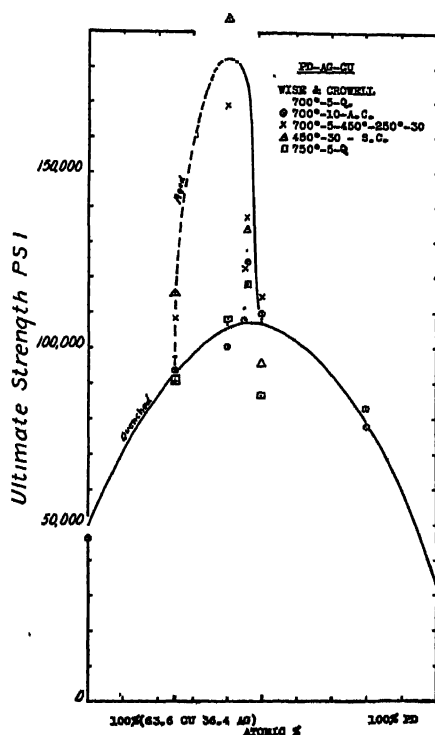


FIG. 22.

involved and suitably chosen alloys quite satisfactorily resistant to oral corrosion.

The color of all of the alloys, suitable in other respects for dental use, is white.

## SECTION II.—INFLUENCE OF PLATINUM AND PALLADIUM UPON MECHANICAL PROPERTIES, OPTIMUM HEAT TREATMENT, COLOR AND COST OF DENTAL ALLOYS

BY WALTER S. CROWELL, E. M. WISE AND J. T. EASH

It has been generally known that the tensile strengths of the quenched gold-base dental alloys and their response to heat treatment were greatly

improved by the addition of platinum. The physical properties of a number of commercial dental alloys were studied a few years ago by R. L. Coleman,<sup>(35)</sup> and studies on the mechanism of the hardening transformation have been made by Oshima and Sachs,<sup>(36)</sup> by Sachs,<sup>(37)</sup> and others, but no systematic study of the nature and magnitude of these effects, as a function of platinum metal content, has been noted.

The analyses reported by Coleman indicate that the composition of commercial alloys is diverse and complex. When calculated to atomic percentage and grouped according to physical properties, however, much of this complexity disappears. Some of Coleman's results, designated by his letters, and the results of tests made on commercial alloys by one of the authors, designated by numbers, are shown in Table 1. These results indicate that when such alloys are heat-treated by commonly accepted methods considerable variations in precious metal content (gold plus platinum group metals) and variations of platinum metal content within the range 9.6 to 18.6 at. per cent occasion little systematic change in tensile properties, although they do influence the melting point, nobility and color. The copper and zinc content seem to be more important in securing high strengths than the factors noted above. The only apparent exception is Coleman's alloy I, which, in spite of its low copper content, develops high tensile properties. Palladium is present in many of the alloys, seemingly without marked effect. Its role, aside from its general action in increasing the melting point, lightening the color and probably improving the workability, is not made clear by these data.

Since the publication of Coleman's paper, the physical properties of precious-metal alloys have keenly interested both dentists and manufacturers of dental products. Recently the manufacturers have endeavored to standardize tests and test methods so that the test results obtained in different laboratories would be comparable.<sup>(38)</sup> While serving as a member of the technical committee working out the methods now accepted, one of the authors was impressed with limited data available regarding the effect of heat treatment, accidental or intentional, on the properties of these alloys in the form of wrought wires, and of the importance of such data to both the manufacturer and the user.

In working out such standard tests, there is a natural tendency to limit the number of specified heat treatments, and to confine them to those which can be accomplished by the user with simple apparatus, and which will be beneficial, or at least not damaging, to the materials tested. Obviously "standard heat treatments" can at best represent but a few of the most frequently encountered conditions of use. Tests of material so treated may not be adequate to indicate clearly the relative or potential merits of the products tested, favoring some, and penalizing others. Furthermore, no evidence will be obtained by such tests of the



TABLE 1.—*Test Data on Commercial Alloys\**

	Analyses by One of the Authors						Coleman's Analyses					
	1	2	3	4	5	A	C	H	I	D	F	J
Atomic per cent												
Pt group.....	18.6	15.7	9.6	16.3	17.0	16.9	15.9	12.1	18.0	7.7	12.8	9.7
Au. . . . .	43.1	44.1	46.2	50.2	39.8	50.2	44.0	46.3	44.7	45.5	48.1	48.9
Ag.....	10.0	11.4	15.2	7.5	17.1	7.0	10.4	13.6	15.0	20.2	22.3	25.2
Cu.....	28.3	28.3	29.0	24.2	25.0	24.0	29.7	28.0	20.7	26.6	16.3	16.1
Zn.....		0.5		1.8	1.1	1.9			1.6		0.06	0.02
Quenched, ultimate tensile strength, lb. per sq. in.....	104,000	113,000	103,500	103,500	124,500	108,000	124,000	113,000	98,000	108,000	102,000	90,000
Quenched elongation, per cent in 8 in. . .	12.0	13.5	16.5	17.5	13.5	12.5	9.6	10.6	12.1	8.8	9.2	10.1
Oven-cooled, ultimate tensile strength, lb. per sq. in.....	154,000	169,000	156,000	153,000	168,000	153,000	175,000	176,000	157,000	138,000	118,000	118,000
Oven-cooled, elongation, per cent in 8 in . .	2.0	4.0	2.0	7.0	2.5	7.5	4.6	0.5	4.6	1.0	6.0	2.2

\* Alloys 1, 2, 3, 4, 5, A, C and I contain both Pt and Pd; D, F, H and J contain platinum only.

range of conditions under which the material tested may give satisfactory results in practice.

From the known constitution of hardenable alloys and from the nature of the precipitation-hardening phenomenon itself, it was certain that a wide range of strengths and ductilities could be developed in a given alloy by heat treatment and that the ductility associated with a particular strength could be altered considerably by a change in heat treatment.

The experiments herein described form a part of the investigation undertaken to supply these much needed data on the combination of properties which can be secured by changes in composition and heat treatment.

The survey of the literature and the data on the binary and ternary systems presented in Section I indicated that the problems involved in these polynary alloys could be much simplified by using atomic per cent composition instead of weight per cent, and by considering the quaternary alloys to be derived from the ternary alloys of the system Au-Ag-Cu by the substitution of platinum and palladium for equal atomic percentages of gold. The composition selected for study was: Au + Pt metals, 50 at. per cent; Ag, 20; Cu, 29; Zn, 1. This type analysis is lower in total gold plus platinum metals than the commonly used dental alloys, but was selected after due consideration of the data available on the ternary systems and with the thought that any differences which might exist between the action of platinum and palladium would be clearly apparent.

Commercial alloys containing larger amounts of precious metals will possess properties that will change to some extent with the precious metal content, owing to the change in the thermal and compositional domain of the precipitable phase and to some slight extent with the change in the nature of the solvent, so that the effects of individual metals will be less clearly indicated.

The type of alloy selected, when free from either platinum or palladium, lies well within the hardenable range as shown in Fig. 20 of Section I, but the corresponding alloy, in which the gold is wholly replaced by palladium, lies slightly outside the hardening range as indicated in Fig. 21 of Section I, so that it was certain that, by increasing the palladium to a sufficiently high level, alloys would be secured that would not be amenable to age-hardening. This nonhardening domain was entered by the alloy containing 30 at. per cent of palladium.

The ternary system Pt-Ag-Cu has not been investigated in detail, but from a consideration of the binaries involved it appears quite certain that the corresponding Pt-Ag-Cu alloy would be hardenable and that the replacement of gold by platinum would not result in the production of nonhardenable alloys.

A small quantity of zinc was introduced to promote soundness and workability. While its presence undoubtedly influences the physical properties, the small quantity present is known to exert only a small effect. The platinum was varied in steps of 5 at. per cent and the series includes alloys up to 20 at. per cent—approximately the limit of workability. The palladium content was likewise increased in steps of 5 at. per cent and this series was extended to include alloys containing 30 at. per cent of palladium. The compositions of the alloys studied in the present research are given in Table 2.

The alloys studied were prepared in accord with high-grade commercial practice and were fabricated by plant-scale equipment and processes. The alloys were prepared by melting accurately weighed charges of component metals of the highest commercial purity. The gold, copper, silver and zinc were at least 99.98 per cent pure, while the platinum was at least 99.9, and the palladium 99.8 per cent pure. The melting losses were negligible, being about 0.1 per cent. The melts weighed 10 oz. each.

TABLE 2. *Wrought Precious-metal Wires*

Alloy No.	96	97	98	99	100	101	102		103	104	105	106
ATOMIC PER CENT												
Pd....		5	10	15	20	25	30	Pt	5	10	15	20
*Au....	50	45	40	35	30	25	20	Au	45	40	35	30
Ag....	20	20	20	20	20	20	20	Ag	20	20	20	20
Cu....	20	20	20	20	20	20	20	Cu	20	20	20	20
Zn....	1	1	1	1	1	1	1	Zn	1	1	1	1
WEIGHT PER CENT												
Pd....		4.0	8.2	12.7	17.6	22.0	26.6	Pt	7.0	14.0	21.1	28.1
Au....	70.8	65.8	60.0	55.0	49.0	42.3	35.2	Au	63.8	56.7	49.6	42.6
Ag....	15.5	16.0	16.6	17.2	17.8	18.5	19.2	Ag	15.5	15.5	15.5	15.5
Cu....	13.2	13.7	14.1	14.6	15.1	15.7	16.4	Cu	13.2	13.3	13.3	13.3
Zn....	0.5	0.5	0.5	0.5	0.5	0.6	0.6	Zn	0.5	0.5	0.5	0.5

The ingots were reduced by swaging to a diameter of 0.067 in. with suitable intermediate anneals, and were then drawn to 0.044 in., annealed and drawn in diamond dies to the final diameter of 0.0395 in. The hard-drawn wires were then carefully straightened and cut into 12-in. lengths. All subsequent heat-treating operations were conducted in a manner adequate to preserve this initial straightness.

#### *Heat Treatments*

The wires were tested after quenching from 600°, 700°, 800°, and in the platinum series, also from 900° C. The most complete studies of aging phenomena were carried out on wires initially quenched from 700° C., although an extensive series of tests was conducted on the platinum content alloys after quenching from 900° C. The 700° C.

quench and the oven-cool treatment are in accordance with the "oven-cool" treatment outlined by the American Dental Trade Association.

The 15-min. aging time was selected with the thought that although it would be too short to develop the maximum properties attainable with many of the alloys, it would more closely correspond with the treatments employed in practice where even shorter treatments are frequently utilized. The brief aging time, emphasizing as it does the relative rates of hardening, gives an excellent indication of the improvement in properties that would be obtained in practice. Age-hardening at a definite temperature for 15 min. is probably more quickly and easily accomplished than is the "oven-cooling" treatment specified by the A.D.T.A. test procedure, and it possesses the very definite advantage of eliminating the effect of all idiosyncrasies in the temperature-time curves of the furnaces employed for oven-cooling.

All of the alloys were aged at 350°, 400°, 450° and 500° C. In many cases supplementary tests at lower aging temperatures were made to develop more fully the trend of the tensile strength aging temperature curve.

In the alloys free from platinum metals the higher aging temperatures undoubtedly are sufficient to completely redissolve the Au-Cu phase, but this is not necessarily true for the alloys containing considerable quantities of the platinum metals, which require aging temperatures of from 400° to 450° C. to develop full hardness in the 15-min. treating period.

Over 360 samples were heat-treated and tested in the course of the present research.

#### *Test Procedure*

Annealing treatments involved the retention of the wire at the desired annealing temperature for 5 min. The wires were water-quenched after annealing.

A vertical tube furnace equipped with three independent heating windings was employed for annealing. By suitably adjusting the currents through the three windings, the temperature throughout the gage length of the specimen could be made uniform within the limits  $\pm 2^\circ$  C. To avoid any possibility of complications that might arise from surface effects, a steam atmosphere was maintained in the furnace—the steam required being supplied by a small auxiliary boiler. A prolongation of the furnace tube extended to within an inch of the surface of the water in the quenching tank.

The specimens to be annealed were hung from a perforated nickel-chromium alloy disk attached to a small tube which extended through a collar closing the top of the furnace. By lifting the tube, the charge of specimens was lifted into the hot zone of the furnace. After the annealing was completed, the supporting tube was quickly lowered to quench

the specimens. By this method almost no surface oxidation occurred and the wires were quite clean and straight after treatment. A thermocouple possessing the same diameter as the wire specimens extended through the supporting tube and was adjusted so that its hot junction was in the plane of the midpoints of the specimens. The heating curve of the thermocouple thus closely approximated that of the specimens.

The constant-temperature aging treatments were performed by placing the samples in a large automatically controlled electric furnace where they were held at the required temperature for 15 min. and were then quenched. A period of 5 min. was required to bring the specimens to the furnace temperature. The oven-cool treatment comprised heating the previously annealed and quenched wires at 450° C. for 5 min. followed by slow cooling to 250° C. in 30 min. The furnace used for this treatment was specially designed to give an almost linear temperature-time curve. The oven-cooled samples were water-quenched when they reached 250° C. This furnace-cooling treatment has been widely used for dental alloys, in spite of the fact that frequently it results in very low ductilities and is quite unsuitable for many alloys—as a matter of fact, it is unreasonable to expect that any one treatment would be suitable for alloys possessing widely differing characteristics.

The tensile properties were determined by means of a small Amsler testing machine arranged so that the full scale range could be varied within the limits of from 100 to 1000 lb. This machine was specially designed to afford speeds sufficiently low to permit the convenient reading of the extensometer.

An Anderson extensometer, reconstructed to provide conical seats for the pivoting pins to eliminate the lost motion characteristic of the commercial instrument, was employed and was very satisfactory. The proportional limit reported is defined as the stress corresponding to the intersection of a prolongation of the nearly straight initial portion of the stress-strain curve with a line possessing a slope, with respect to the load axis, 25 per cent greater than the straight initial portion of the curve and tangential to the stress-strain curve. This value is much lower than that usually called the yield point in engineering parlance.

The elongations were all measured on an 8-in. gage length and were determined with the aid of a B. & L. toolmakers' microscope.

#### *Properties of the Annealed and Quenched Alloys*

Triplicate samples of all of the alloys were annealed for 5 min. at 600°, 700° and 800° C., and in addition a 900° C. treatment was applied to the platinum series. All samples were promptly water-quenched from the annealing temperature.

The results for the alloys containing palladium are summarized in Figs. 23 and 24. Tensile strength increases regularly with the palladium

# THE ROLE OF THE PLATINUM METALS IN DENTAL ALLOYS

ent and falls rather gradually with an increase in annealing temperature within the range 600° to 800° C. The elongations remain close 0 per cent for samples annealed at 700° or 800° C., with the exception of the alloy containing 30 at. per cent Pd, which requires 800° C. to develop its normal ductility. The samples annealed at 600° C. develop a gradual reduction in elongation with an increase in palladium content. Doubtless this is due to the reduction in grain size with an increase in palladium content.

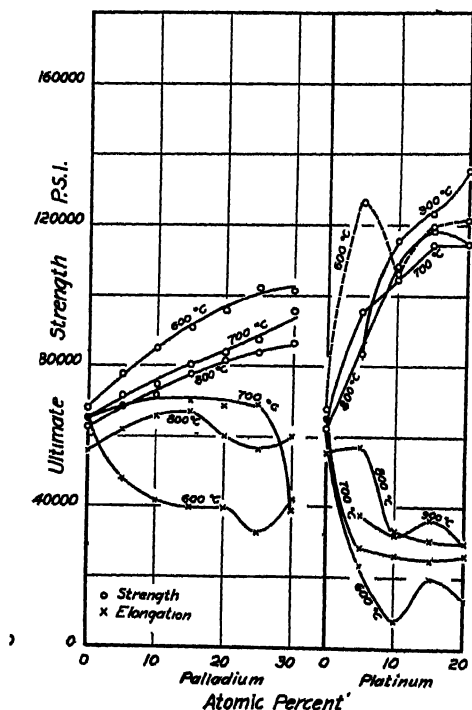


FIG. 23.

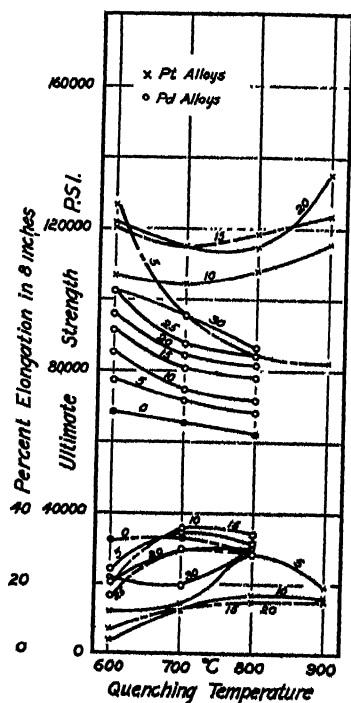


FIG. 24.

FIGS. 23 AND 24.—INFLUENCE OF PLATINUM METAL CONTENT AND QUENCHING TEMPERATURE UPON PROPERTIES OF UNAGED ALLOYS.

The results for the platinum-content alloys are summarized in Figs. 23 and 24. The tensile strength rises very rapidly upon the addition of even small amounts of platinum, particularly in the samples annealed at 600° C. The 600° C. series is rather irregular and the 5 per cent platinum alloy appears anomalously high. Probably this is due to the inheritance of some slight effects resulting from plant processing, for this is not evident at higher annealing temperatures. Increasing the annealing temperature from 600° to 700° C. produces a lowering of

strength, as was the case with the palladium alloys, but further increases in annealing temperature to 800° and 900° C. result in a pronounced increase in the strength of all of the alloys except the one containing 5 at. per cent Pt. This effect occurs to a slight extent with the silver-rich copper-silver alloys and is due to the increase in the hardness of the solid solution occasioned by the solution of increased quantities of a second phase.

The tensile strength of the 20 at. per cent platinum alloy reaches 135,000 lb. per sq. in. when quenched from 900° C., a value more than twice that of the annealed platinum-free gold-base alloy and higher than many of the aged alloys.

The elongations of the platinum-content alloys increase quite regularly with the quenching temperature. The reduction in elongation with increasing platinum content, noted at the low annealing temperatures, is doubtless due to the very considerable amount of the hard platinum-rich phase present after annealing at these low temperatures, and to incomplete recrystallization.

#### *Properties of Alloys, Annealed, Quenched and Aged at Constant Temperatures*

The tensile properties of the palladium-content alloys annealed at 700° C. for 5 min., quenched and aged for 15 min. at temperatures ranging from 200° to 500° C. are shown in Figs. 25 and 26. The maximum tensile strength increases rather rapidly with the palladium content up to a palladium content of 25 at. per cent. The maximum strength of the alloy containing 25 at. per cent Pd aged at 450° C. for 15 min. reaches the very respectable value of 147,000 lb. per sq. in. Increasing the palladium content much above this causes an abrupt fall in the response to precipitation heat treatments due to the shift in the composition domain of the precipitable phase.

The rise in the temperature required to produce maximum strength in a fixed time undoubtedly is due to the change in the composition of both the precipitate and the solvent, while the temperature over which the alloys are supersaturated undoubtedly is raised by the addition of palladium. The net result of these changes is reflected in the tensile strength-aging temperature curves shown in Fig. 25.

The increase in aging temperature required to produce the maximum strength is pronounced for palladium contents up to a value between 5 and 10 at. per cent, and is very slight thereafter. This strongly suggests that the dominant hardening constituent in the alloys containing 10 or more at. per cent of palladium is Pd-Cu, probably containing some gold in solid solution. The formation of Au-Cu seems to be almost completely suppressed in the 25 at. per cent palladium-content alloy.

Increasing the quenching temperature from 700° to 800° C., followed by aging at 450° C., results in only a small loss in strength of the 25 at. per cent alloy. The change in the electrical resistivity resulting from this increase in quenching temperature is also slight. It appears, therefore, that the palladium-content alloys are quite homogeneous after quenching from temperatures as low as 700° C.

As a result of these phenomena, the tensile strength-aging temperature curves of the alloys containing from 5 to 20 at. per cent of palladium

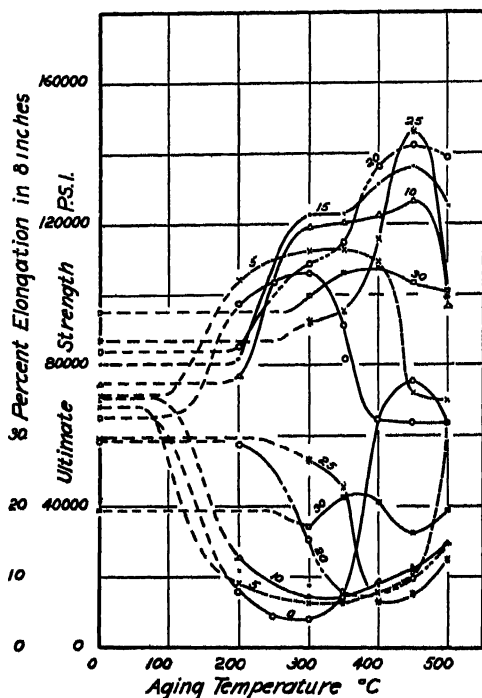


FIG. 25.—EFFECT OF AGING TEMPERATURE AND PALLADIUM CONTENT ON PROPERTIES OF ALLOYS INITIALLY QUENCHED AT 700° C.

show relatively flat maxima and in consequence, strengths quite close to the maximum will be obtained in spite of considerable departures from the best aging temperature for the particular alloy. In other words, the hardening is rendered more nearly foolproof than it is with alloys containing a single precipitable phase.

The elongations of the palladium-content alloys containing up to 25 at. per cent, after quenching from 700° C., are all high, some 35 per cent. Aging produces a considerable reduction in the elongation, which drops to its minimum value at an aging temperature at or slightly below that producing the highest strength. However, none of the palladium-content alloys exhibit elongations less than 5 per cent after aging for 15 min.



at temperatures ranging from 200° to 500° C., although the elongation of the palladium-free alloy drops to about 4 per cent after aging at 300° C. The alloy containing 30 at. per cent of palladium shows only minor changes in ductility, which are but a reflection of the small changes in tensile strength occasioned by aging this alloy.

The tensile properties of the platinum-content alloys quenched from 700° C. and subsequently aged for 15 min. at various selected temperatures are shown in Figs. 26 and 27. It will be noted that the strengths of these alloys after aging at 400° to 450° C. increase rapidly with the plat-

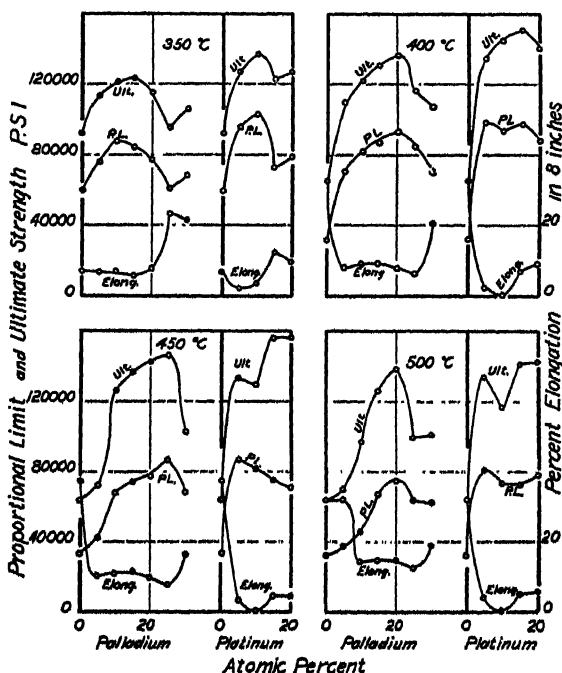


FIG. 26.—PROPERTIES OBTAINED BY ANNEALING AT 700° C., QUENCHING AND AGING 15 MIN. AT TEMPERATURES INDICATED.

inum content up to some 15 at. per cent Pt, and that the tensile strengths of the alloys containing 15 or 20 at. per cent Pt attain a value of 156,000 lb. per sq. in. after aging for 15 min. at 450° C.

Increasing the platinum content above 15 at. per cent produces no further effect upon the tensile strength of alloys quenched from 700° C. and subsequently aged for 15 min. at constant temperatures. This is undoubtedly due to the fact that only a portion of the platinum is dissolved in the predominating solid solution at this low quenching temperature.

The platinum-content alloys are less ductile than the palladium-content alloys after quenching from 700° C., but their ductility increases

with an increase in annealing temperature. The age-hardening treatment produces a marked reduction in the elongation of the alloy containing 10 at. per cent Pt, and to a lesser extent that of the remaining alloys. The alloys containing 15 and 20 at. per cent Pt show less marked reductions in elongation, possibly due to the presence of some of the copper in the platinum-rich phase, and as a result a reduction in the amount of copper in the hardenable matrix.

In order to observe the influence of platinum when present in solution in the predominating solid solution, a series of samples were annealed

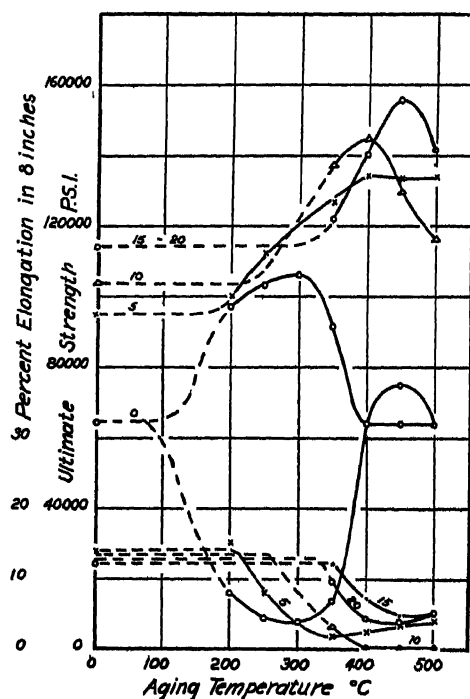


FIG. 27.—EFFECT OF AGING TEMPERATURE AND PLATINUM CONTENT ON PROPERTIES OF ALLOYS INITIALLY QUENCHED AT 700° C.

at 900° C. for 5 min., quenched, and subsequently aged for 15 min. at temperatures ranging from 300° to 500° C. Owing to the fact that the solidus of the alloy containing only 5 at. per cent Pt is very close to 900° C., samples of this alloy annealed at 800° C. were included in this new series of tests. The results are summarized in Fig. 28. Increasing the annealing temperature from 700° to 900° C. results in an increase in the tensile strength of the quenched alloys containing upwards of 5 at. per cent Pt, as previously noted; and likewise increases the elongation in alloys containing 10 or more atomic per cent of platinum.

The aging temperature required to produce the maximum strength for these alloys upon aging for 15 min. appears to be very close to 400° C. for the alloys containing up to 10 at. per cent Pt and 425° C. for the 15 and 20 at. per cent platinum alloys, about 25° below that found desirable for the high-palladium alloys. Some slight irregularities in the curves shown in Fig. 28 will be noted, the alloy containing 15 at. per cent Pt being notable in this respect.

The maximum tensile strengths attained in alloys quenched from 900° C. and subsequently aged increase rather rapidly with the platinum

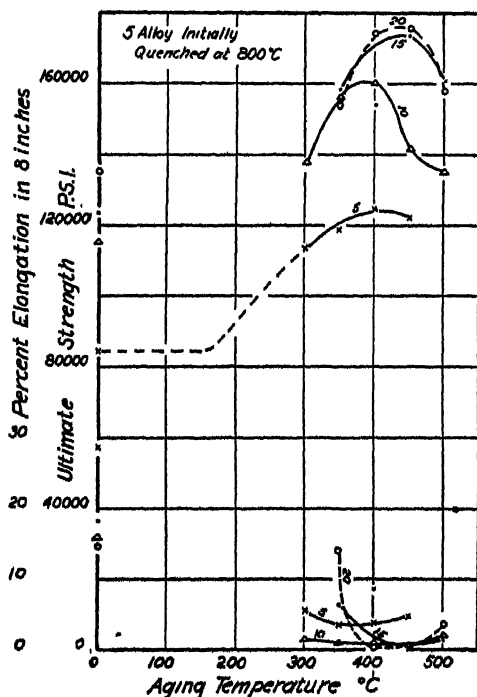


FIG. 28. —EFFECT OF AGING TEMPERATURE AND PLATINUM CONTENT ON PROPERTIES OF ALLOYS INITIALLY QUENCHED AT 900° C.

content up to 10 at. per cent Pt and then more slowly up to 20 at. per cent, the limiting composition studied, at which platinum content a tensile strength of over 175,000 lb. per sq. in. is attained.

The elongations of the alloys fall markedly upon aging, as is usual with age-hardening alloys.

With the alloys of very high platinum content the possibility of precipitating a platinum-content phase, such as Pt-Au or Pt-Ag, becomes possible, for it will be recalled that the solubility of platinum in gold or in silver falls below 20 at. per cent at low temperatures. The presence of copper, however, would tend to increase this solubility slightly in

alloys containing considerable gold, while palladium would be even more effective. In the alloys containing less than 15 at. per cent Pt, the possibility of precipitating phases other than those based on Pt-Cu or Au-Cu seems remote. In the palladium-content alloys the situation is different because palladium forms a continuous series of solid solutions with gold and with silver, so that the only phases precipitated would be those based on Au-Cu and Pd-Cu. The nature of the quaternary systems will be further discussed in a later communication.

No comment has been made regarding the reason for the fall in strength occasioned by increasing the aging temperature beyond that producing the maximum strength. This behavior is characteristic of all age-hardening alloys and is due primarily to the formation of a gross precipitate, which is an ineffective hardener. Moreover, with the precious-metal alloys containing Au-Cu, Pd-Cu, and to a lesser extent Pt-Cu, a moderate elevation of temperature above that required to produce maximum strength is sufficient to wholly redissolve the precipitated phase.

*Properties Developed by Annealing at 700° C., Quenching, Reheating to 450° C., and Oven-cooling*

The tensile properties of the palladium and the platinum-content alloys developed by annealing at 700° C. for 5 min., quenching and reheating at 450° C. for 5 min., followed by slow cooling to 250° C. in 30 min. and then quenching, are shown in Fig. 29. The alloys of the palladium series show a rapid rise in strength up to 10 at. per cent Pd, followed by a slower rise up to 20 at. per cent, at which point a tensile strength of 145,000 lb. per sq. in. is attained. Increasing the palladium content beyond this value results in a decrease in aged strength upon slow cooling.

The elongations obtained are shown in the same figure. These reflect to some extent the strengths attained and decrease with the addition of palladium up to 15 at. per cent and thereafter increase. The minimum values are about 2.7 per cent.

The tensile strengths of the platinum-content alloys after annealing at 700° C. and oven-cooling are also presented in Fig. 29. The tensile strength shows a general increase with the platinum content and a strength of 160,000 lb. per sq. in. is attained by the alloys containing 15 to 20 at. per cent Pt. The strength of the wire containing 10 at. per cent Pt is anomalously low, apparently a reflection of some small difference in the previous thermal history of this wire which was incompletely effaced by the low (700° C.) initial anneal.

The elongations reach a minimum at 5 to 10 at. per cent Pt but are much higher in the alloys containing 15 and 20 at. per cent Pt.

This particular heat treatment, an initial quench from 700° C. followed by reheating to 450° C. and cooling to 250° C. in 30 min., has been widely used in testing dental alloys, so that it has been thought desirable

to compare the strength and ductility obtained by this means with that obtained by other thermal treatments. This comparison can be made by comparing the strengths and ductilities of the several alloys when aged for 15 min. at the temperature producing the maximum strength, with the strengths and ductilities produced by the above mentioned 700° C. anneal followed by oven-cooling. These data are presented in Fig. 30.

For the alloys containing between 3.5 and 21.5 at. per cent Pd, the 35-min. treatment involving slow cooling produces a tensile strength slightly in excess of that obtained by a 15-min. treatment at a fixed tem-

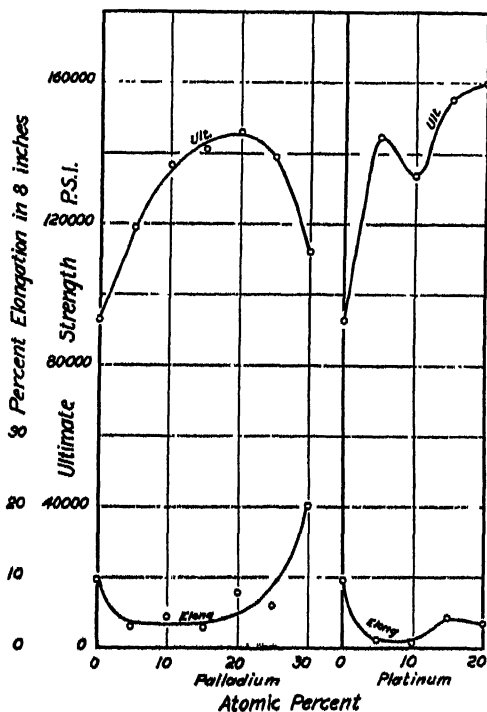


Fig. 29.—PROPERTIES OBTAINED BY ANNEALING AT 700° C., QUENCHING AND OVEN-COOLING FROM 450° TO 250° C. IN 30 MINUTES.

perature, but generally less than that obtained by aging for 1 hr. at 400° C. (for alloys containing from 10 to 25 at. per cent Pd). The ductilities resulting from the oven-cool treatment applied to alloys containing from 2.5 to 24 per cent Pd are much lower than those produced by either the 15-min. constant-temperature treatment or the 1-hr. or 4-hr. treatments. This is particularly noticeable in the alloys containing 10 to 15 at. per cent Pd, where the ductility resulting from oven-cooling is about one-third that produced by the 15-min. treatment and less than one-half that resulting from a 1-hr. treatment at 400° C. In passing, it may be noted that increasing the time of aging at 400° C. to 4 hr. results in a still

further increase in strength in the alloys containing between 10 and 25 at. per cent Pd, and that this increase in strength is associated with only a very slight further change in ductility. On the whole, it appears that the oven-cooling treatment is ill adapted to fully develop the properties of palladium-content alloys.

The platinum-content alloys show a somewhat different behavior, for the strengths resulting from the 15-min. aging treatment, following a 700° C. quench, are nearly the same as those resulting from oven-cooling,

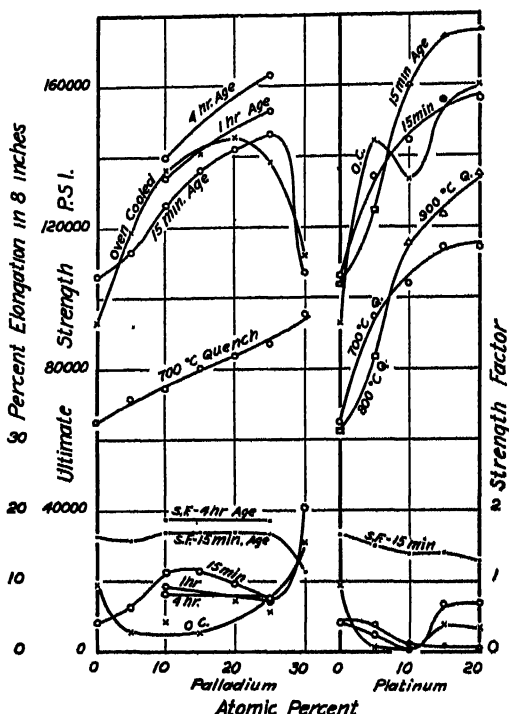


FIG. 30.—COMPARISON OF PROPERTIES OBTAINED IN ALLOYS CONTAINING VARIOUS AMOUNTS OF PLATINUM METALS BY OVEN-COOLING OR BY AGING FOR 15 MIN. AT OPTIMUM TEMPERATURES.

while the ductilities resulting from oven-cooling are generally only slightly lower. The maximum strength attained (160,000 lb. per sq. in. in the 20 at. per cent Pt alloy) does not represent the maximum obtainable from alloys containing a very high platinum content, for such alloys when free from palladium require brief anneals at temperatures considerably above 700° C. for the full utilization of their platinum content.

By increasing the quenching temperature to 900° C. for the alloys containing 10 or more atomic per cent of platinum, higher strengths can be obtained than those resulting from a 700° C. initial anneal followed by aging. For the 20 at. per cent alloy the difference between strength

of the alloy quenched from 900° C. and aged for 15 min. at the proper temperature and the same alloy annealed at 700° C., quenched and then aged at the proper temperature for 15 min. is 20,000 lb. per sq. in., while the gain over oven-cooling is 15,000 lb. per sq. in. This increase in strength is associated with a considerable loss in ductility, but it is probable that quenching from a temperature slightly below 900° C. would lead to the production of nearly the same strength coupled with higher ductility. It is also probable that the introduction of some palladium would increase the ductility and permit the use of lower quenching temperatures.

The adherence to a scheme that limits the initial quenching temperature to a definite value and the use of an arbitrary aging treatment seems undesirable and tends to restrict unnecessarily the designer of dental alloys in his effort to secure the best possible result, and if used by investigators in studying the behavior of dental alloys may lead to erroneous conclusions regarding the influence of the platinum metals upon the properties of such alloys.

A question naturally arises concerning the limitation of quenching temperature by the melting of solders which might be used to unite parts prior to heat treatment. It so happens that the much better white solders can be secured if their melting points be raised, so that the feasibility of increasing the quenching temperatures of the white alloys seems altogether reasonable.

#### *Relation between Tensile Strength and Elongation as Determined by Platinum Metal Content and Thermal Treatment*

The tensile strengths and elongations resulting from the replacement of various amounts of gold by palladium or platinum and the application of a variety of heat treatments are summarized in Fig. 31.

The elongations resulting from quenching from 900° C., without subsequent aging, range from 15 to 18 per cent in the case of the alloys containing from 10 to 20 at. per cent Pt, while the tensile strength rises with the platinum content from 115,000 to 135,000 lb. per sq. in.

The elongations resulting from quenching at 700° C. range from about 20 to 35 per cent in the alloys containing from 0 to 30 at. per cent Pd. The strength rises almost directly with the palladium content and reaches about 95,000 lb. per sq. in. in the alloy containing 30 at. per cent Pd.

The elongations of the palladium-content alloys quenched from 700° C. and subsequently aged for 15 min. at the temperature producing the maximum strength increase with the palladium content up to 15 at. per cent and then decrease up to 25 at. per cent Pd. The strengths attained as a result of the aging treatment increase almost directly with the palladium content up to 25 at. per cent Pd and attain 147,000 lb. per sq. in. with this palladium content.

The strengths of the platinum-content alloys initially quenched from 900° C. and subsequently aged for 15 min. at the temperature producing the maximum strength increase rapidly with the platinum content up to 20 at. per cent Pt, the limit of the present series. At this platinum content a tensile strength of 175,000 lb. per sq. in. is attained. The ductilities decrease gradually with the platinum content up to 10 at. per cent. Beyond this point no definite trend is indicated.

The strength resulting from oven-cooling the palladium-content alloys,

initially annealed at 700° C., rises rapidly with the palladium content up to 20 at. per cent Pd, at which composition a strength of 145,000 lb. per sq. in. is attained and then decreases with a further increase in palladium content. The elongations are almost constant over the range 5 to 15 at. per cent Pd but increase rapidly with a further increase in palladium content.

The strength resulting from oven-cooling the platinum-content alloys, initially annealed at 700° C., varies rather irregularly with the platinum content, because of the differences in the initial state of the alloys which are not effaced by annealing at this low temperature. The ductilities show an upward trend over the range 10 to 20 at. per cent Pt and reach a value of about 3.5 per cent at this limiting composition.

In general, it is evident that the attainment of strengths greater than 106,000 lb. in the type of alloy studied requires the presence of either platinum or palladium and that the attainment of strengths in excess of 150,000 lb. per sq. in. by aging

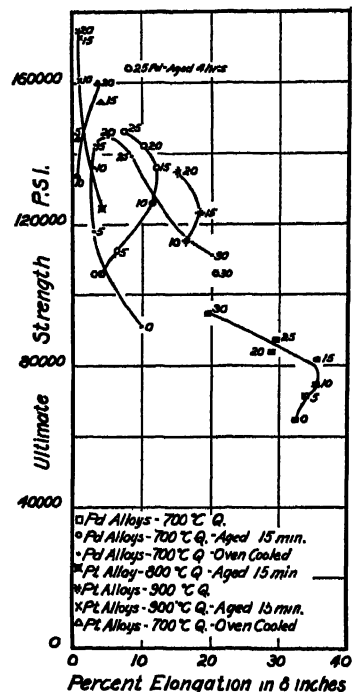


FIG. 31.—RELATION BETWEEN STRENGTH AND DUCTILITY AS DETERMINED BY PLATINUM METAL CONTENT AND HEAT TREATMENT.

for 15 min. requires the presence of platinum, although by increasing the aging time strengths in excess of 160,000 lb. per sq. in. can be secured with palladium alone.

The ductilities at given levels of strength are, on the whole, higher with the palladium-content alloys. However, the excellent combination of strength and ductility secured by merely quenching the alloys of high platinum content from 900° C. is an exception to this.

Relations such as those shown in Fig. 31 are very useful to designers of dental alloys, for they indicate directly the type composition and platinum metal content required to secure the strength and ductility



*Relation between Physical Properties and Length of Aging Period*

Due to the fact that the aging period employed for the major portion of the work was relatively short—15 min.—it seemed desirable to determine the effect of longer aging periods upon the physical properties of a few of the alloys. Accordingly, three alloys containing 10 and 25 per cent Pd and 20 per cent Pt, respectively, were annealed and quenched, and then aged for periods of 15 min., 1 hr. and 4 hr. at 400° C. The palladium alloys were initially annealed for 5 min. at 700° C., while the platinum alloy was annealed for 5 min. at 900° C., and all were water-quenched from the annealing temperature.

The results obtained are shown in Fig. 32. In the case of the palladium alloys the rapid increase in the tensile strength up to 1 hr. is followed by a gradual increase up to 4 hr. From the shape of the curves it is evident that a further increase in time would produce even higher strengths. A strength of 163,000 lb. per sq. in. was obtained for the 25 per cent Pd alloy after the 4-hr. treatment. The tensile strength of the 20 per cent Pt alloy reached a maximum of 179,000 lb. per sq. in. after a 1-hr. aging treatment and then decreased with a further increase in time.

The reduction in strength observed with platinum alloy, resulting from the 4-hr. treatment is due to overaging and would not occur in this period of time if the aging temperature were lowered very slightly below 400° C.

The relative rates of aging are brought out more clearly by considering the proportion of the maximum observed strength attained after aging at the several time periods employed. These curves are shown in Fig. 32. The platinum alloy attains 97.5 per cent of its maximum observed strength in 15 min., while the 10 at. per cent Pd alloy attains 88.2 per cent of its maximum strength in 15 min., and the 25 at. per cent Pd alloy 71.2 per cent of its maximum strength in 15 minutes.

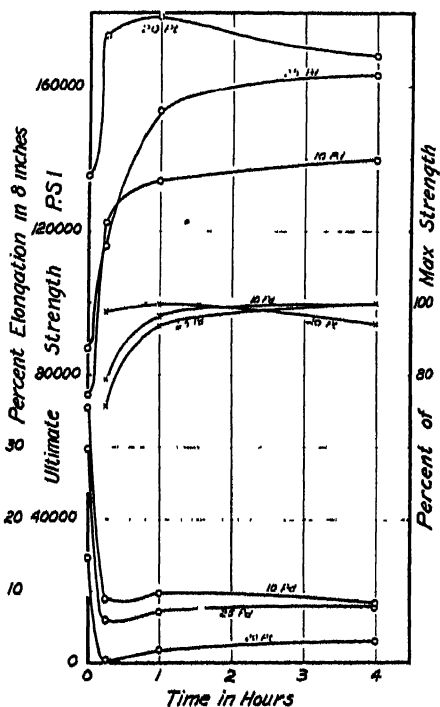


FIG. 32.—INFLUENCE OF AGING TIME (400° C.) UPON THE PROPERTIES.

From these observations it is evident that at 400° C. the rate of precipitation and subsequent coalescence (the latter causing a reduction in strength) is slightly higher with the platinum alloy than with the palladium-content alloys. This is, in general, in accord with conclusions which result from a consideration of the strength vs. aging-temperature curves, where it has been noted that the optimum aging temperatures for the platinum-content alloys are slightly below those for the corresponding palladium-content alloys. Increasing the aging temperature increases atomic mobility and is, for this reason, within a limited range, roughly equivalent to an increase in time. It must not be forgotten that the solubility of the precipitable phase increases with the temperature, and as a result the degree of supersaturation is reduced by increasing the aging temperature. For this reason an upper limit is placed upon the aging temperature regardless of the brevity of the aging treatment employed.

The elongations of all of the alloys decrease abruptly with the onset of the precipitation, but in general attain their minimum values *earlier* in the aging process than the point corresponding to the maximum strength. This is important in view of the fact that it demonstrates that by fully aging better combinations of strength and ductility can be secured than by aging slightly less than is required to produce the maximum strength.

The ductilities of the two palladium alloys aged at 400° C. are much higher than the platinum alloy. This relation holds also with alloys age-hardened by other thermal cycles.

#### *Strength Ratios Which Can Be Secured by Age-hardening*

The ratio between the strengths of the aged and quenched palladium-content alloys is remarkably constant and lies between 1.54 and 1.7, for alloys containing from 0 to 25 at. per cent Pd with constant copper and silver contents, aged 15 min. at the temperature producing the maximum strength. The strength factor curve is indicated in Fig. 30. For longer aging times the ratio is higher, being about 1.9 for a 4-hr. treatment at 400° C.

For the platinum series the ratio is 1.49 for the 5 at. per cent Pt alloy quenched from 800° C., while it drops to 1.4 for the 10 and 15 at. per cent Pt alloys and to 1.3 for the 20 at. per cent alloy quenched at 900° C.

The decrease in the hardening ratio of the high-platinum alloys is due largely to residual heterogeneity, possibly supplemented by abnormally high quenching strengths, the result of some slight precipitation during the quench.

From the nature of the aging process and the general similarity in the mode of formation of Au-Cu, Pd-Cu and Pt-Cu, these relations were not unexpected, but are nevertheless interesting and valuable.

The strength ratios which can be secured in other alloys may well be considered in this connection. For duralumin they are about 1.36; for the copper-nickel-iron alloys they are roughly 1.7; for aluminum (K) monel they may run about 1.9; while with the austenitic steels containing titanium they are about 1.9. It should be noted that the attainment of these ratios requires heat treatments of many hours' duration. In view of this, it appears that the age-hardening dental alloys are exceptionally responsive to age-hardening, particularly to brief heat treatments, and that many of them are unique in the small difference between the quenching and aging temperatures required to develop high strengths.

### *Domain of the High-strength White Alloys*

The addition of palladium rapidly eliminates the greenish yellow color characteristic of the gold-silver-copper alloy. The presence of as little as 5 at. per cent Pd serves to produce a rather pale yellow color, while the addition of 10 at. per cent produces further whitening, although the yellow color is still evident. The addition of 15 at. per cent Pd results in an alloy which could be called white, although its color is distinctly less white than that characteristic of alloys containing from 20 to 30 at. per cent Pd. Fortunately, the physical properties obtainable with alloys with a palladium content, ranging from 15 to slightly above 25 at. per cent are excellent, so that alloys within this range are not only white but strong, and in consequence, permit the construction of very inconspicuous restorations.

In cases where strengths in excess of 150,000 lb. per sq. in. are required, the simple quaternary palladium, gold, silver and copper alloys may be modified by the addition of small quantities of platinum to further strengthen them.

The platinum-content alloys are less white than the corresponding palladium alloys, and even the alloy containing 20 at. per cent Pt possesses a distinctly dark color. Quenching from 900° C. to dissolve more of the platinum-containing phase improves the color to a slight extent, but it still remains less white than that of the corresponding palladium alloy.

It appears, therefore, that palladium, sometimes in conjunction with smaller quantities of platinum, is best suited to the production of the very white, strong alloys, while platinum is more appropriate for the high-strength yellow gold alloys.

### *Economics Resulting from Use of Alloys Containing Platinum Metals*

The sizes of the structural members of a dental restoration are important and for esthetic and practical reasons it is highly desirable that they be kept down to a minimum. This naturally suggests the use of high-strength alloys containing the platinum metals. However,

even if no premium is placed upon size other than that it be adequate to withstand the stresses imposed, it develops that the actual metal cost to produce the structure is reduced by the replacement of a considerable portion of the gold by either platinum or palladium. This is demonstrated in Fig. 33, where the relative strengths attained by 15-min. aging treatments at optimum temperatures are indicated; the properties of the alloy free from platinum metal, aged at 300° C., being considered to be 100 per cent in all cases.

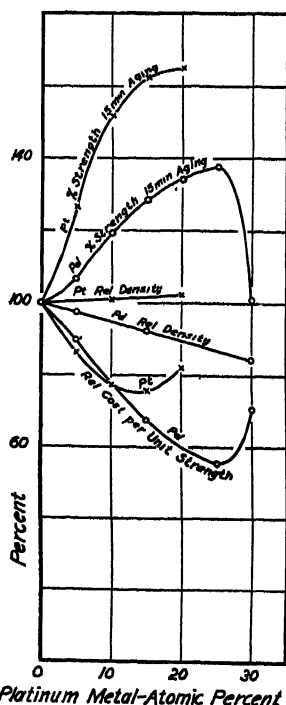


FIG. 33.—RELATIVE STRENGTHS AND COSTS PER UNIT STRENGTH OF ALLOYS AS DETERMINED BY THEIR PLATINUM METAL CONTENT.

The relative densities compared to the gold-base alloy are also indicated. The pronounced reduction in density occasioned by the introduction of palladium is particularly interesting.

The relative cost of metal to produce a structure of fixed tensile strength is indicated. This cost *decreases* with the replacement of part of the gold by either platinum or palladium. With platinum the cost reaches a *minimum* at 15 at. per cent Pt, while with palladium it continues downward to about 25 at. per cent Pd. The costs are equal for platinum or palladium at the 10 at. per cent level, but diverge slightly either side of this point.

It is a fortunate circumstance that the particularly desirable alloys are white in color, as this, in conjunction with the small sections required, aids materially in the production of very inconspicuous restorations.

#### EFFECT OF PLATINUM METALS ON THE GRAIN SIZE

As a result of metallographic investigations it was found that the effect of an increase in the palladium content on the structure of the annealed and quenched alloys is to decrease the grain size without resulting in the production of a new phase. This decrease in grain size is directly related to the increase in the melting point of the alloys.

The high-platinum content alloys, however, are characterized by a very fine duplex structure. One phase is a ductile platinum-rich constituent which elongates on rolling and causes the formation of a very fine fibrous structure. The duplex alloys are very resistant to grain growth so that even after the high-temperature heat treatments the fine

fibrous structure is maintained. Additions of moderate amounts of platinum also produce a very fine grain size in the alloys that are homogeneous.

The effect of the platinum metal additions on the microstructure of the alloys is in excellent agreement with the improvements in physical properties that are reported herein.

#### SUMMARY AND CONCLUSIONS

A careful survey has been made of the tensile properties of two series of quaternary alloys, containing gold, silver, copper, and either platinum or palladium, to determine definitely the properties that can be developed by the application of judicious and other heat treatments. This work has led to the following conclusions:

1. The general nature of the age-hardening transformation is much the same whether the hardening agent is Au-Cu, Pd-Cu or Pt-Cu.

2. The introduction of either platinum or palladium, particularly the former, results in a considerable increase in solid solution hardness, and at the same time permits the multiplication of the strength through age-hardening by substantially the same ratios as those obtainable with the weaker gold-silver copper alloys. The increase in strength resulting from the introduction of platinum or palladium is accompanied by a marked increase in melting point, while the increase in strength resulting from the addition of further quantities of base-metal hardeners such as copper and zinc occasions not only a decrease in melting point but also a rather serious loss in nobility.

3. The aging temperature required to produce the maximum strength in a definite time interval has been determined for each of the alloys. For 15-min. treatments this temperature is 300° C. for the gold-base alloy free from platinum or palladium, while it rises to about 450° C. in alloys containing large percentages of either platinum or palladium.

4. It has been demonstrated that by the introduction of the proper quantities of platinum or palladium, alloys can be produced which will develop excellent properties in spite of a considerable deviation from the optimum age-hardening temperature. In other words, such alloys possess a broad hardening range and are reasonably foolproof.

5. The results obtained by quenching from 700° C. and oven-cooling are compared with those obtained by aging at fixed temperatures, and the superiority of the fixed temperature-aging treatment is demonstrated. This superiority is particularly evident with the palladium-content alloys.

6. The influence of quenching temperature upon the properties of the platinum-content alloys was investigated, and it is shown that the strengths of the high-platinum alloys can be greatly increased by quenching them from a high temperature.

7. The rates of hardening in alloys containing platinum and those containing palladium are compared, and the somewhat higher rate characteristic of platinum is shown.

8. The domain of the hardenable high-strength white alloys is indicated.

9. The economies resulting from the replacement of considerable quantities of gold by either platinum or palladium are indicated, and it is shown that savings in metal cost as high as 40 per cent can be secured by this means.

10. Both palladium and platinum reduce the grain size of the alloys, platinum being the most effective. Platinum likewise leads to the development of a duplex fibrous structure in the wrought alloys.

#### ACKNOWLEDGMENTS

The authors are indebted to Mr. E. A. Joline, vice-president, The S. S. White Dental Mfg. Co., and to Mr. A. J. Wadhams, manager of the Development and Research Department of the International Nickel Co., for permission to publish the results of this investigation, and to Dr. P. D. Merica, technical advisor to the president of the International Nickel Co., for his helpful advice and encouragement.

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[Appendix on next page]

## DISCUSSION

(T. A. Wright presiding)

W. SOUDER, G. C. PAFFENBARGER and W. T. SWEENEY, Washington, D. C. (written discussion). The first half of this paper represents one of the most valuable compilations of metallurgical data on the platinum metals and alloys we have ever seen. The authors have been careful to give credit for the equilibrium diagrams which they have reproduced and have added some new diagrams which are very informative. If we have correctly summarized the second half of the paper, it shows that platinum metals may be used in dental alloys and similar alloys with certain advantages. They have shown the effects of varying percentages of these alloys when they are substituted for gold in a basic formula.

Our first observation is that the alloys reported do not represent the highest grade of dental alloys now available, if we judge them by high ultimate tensile strength and high percentage elongation. In looking over some data now before us, which are to be published soon, we find several commercial dental alloys having 170,000 to 180,000 lb. per sq. in. ultimate tensile strength and elongations of 4 to 6 per cent. These alloys are not low in noble-metal content, as is hinted in conclusion 2. We feel that the superior qualities of these commercial dental alloys result from a more skilful arrangement of the copper, silver and zinc ratios in alloys of approximately the same precious-metal content as those reported in this paper. We heartily agree with the authors'

## APPENDIX

TABLE 3.—Testing Data on the Dental Alloys

Composition Atomic Percent	Atomic Percent Pt	Quenching Temperature °C.	Annealing Temperature °C.	Ultimate Strength lbs./sq. in.	Proportional Limit lbs./sq. in.	Percent Elongation in 8 inches
0	0	600	-	67,900	40,800	32.1
5	-	600	-	77,300	46,400	24.0
10	-	600	-	84,900	51,100	21.0
15	-	600	-	90,900	61,600	19.2
20	-	600	-	95,800	61,700	20.0
25	-	600	-	102,000	67,400	16.3
30	-	600	-	101,600	68,000	27.2
-	5	600	-	126,700	84,000	11.7
-	10	600	-	106,500	68,700	3.8
-	15	600	-	120,000	60,700	10.0
-	20	600	-	121,400	63,600	6.9
0	0	700	-	65,000	40,500	32.6
5	-	700	-	71,400	43,000	34.2
10	-	700	-	74,800	42,400	33.5
15	-	700	-	80,800	44,300	35.1
20	-	700	-	83,900	44,600	29.3
25	-	700	-	87,300	42,900	29.6
30	-	700	-	98,600	59,200	19.6
-	5	700	-	98,100	61,700	14.1
-	10	700	-	104,300	64,400	13.3
-	15	700	-	114,700	64,300	12.4
-	20	700	-	114,400	50,000	13.2
0	0	800	-	61,400	37,800	27.7
5	-	800	-	68,300	41,800	31.0
10	-	800	-	71,600	41,300	32.6
15	-	800	-	77,900	39,400	33.5
20	-	800	-	81,300	40,600	29.8
25	-	800	-	83,900	42,400	28.2
30	-	800	-	86,200	43,200	30.0
-	5	800	-	83,900	48,200	28.6
-	10	800	-	108,200	64,300	16.5
-	15	800	-	118,200	52,500	15.3
-	20	800	-	114,700	56,300	14.7
-	5	900	-	82,200	53,800	12.9
-	10	900	-	115,600	59,800	16.0
-	15	900	-	123,600	68,100	18.3
-	20	900	-	135,100	83,200	14.6
0	0	700	200	97,600	68,800	8.1
5	-	700	200	103,900	67,000	9.3
10	-	700	200	77,300	50,500	12.8
15	-	700	200	82,400	61,500	11.0
20	-	700	200	85,200	49,600	28.9
-	5	700	200	100,200	71,600	18.4
0	0	700	250	103,800	73,900	4.7
-	5	700	250	112,900	80,000	8.1
0	0	700	300	106,300	67,600	4.3
5	-	700	300	112,400	69,500	6.5
10	-	700	300	119,800	75,000	7.3
15	-	700	300	123,000	78,300	9.2
20	-	700	300	108,900	64,000	15.2
25	-	700	300	92,500	57,100	26.6
30	-	700	300	100,100	62,000	17.1
0	0	700	350	92,100	59,600	7.1
5	-	700	350	113,000	75,800	6.4
10	-	700	350	120,900	87,000	7.0
15	-	700	350	125,400	84,400	5.4
20	-	700	350	115,100	78,100	8.0
25	-	700	350	95,300	61,200	23.1
30	-	700	350	106,400	69,800	21.5
-	5	700	350	127,200	95,200	1.9
-	10	700	350	137,700	103,600	3.4
-	15	700	350	122,900	78,100	12.4
-	20	700	350	126,700	78,500	9.8
0	0	700	400	64,800	32,200	32.1
5	-	700	400	109,700	70,200	8.0
10	-	700	400	122,300	81,800	9.5
15	-	700	400	130,800	87,000	9.2
20	-	700	400	134,800	93,600	8.0
25	-	700	400	116,100	84,700	6.6
30	-	700	400	107,500	70,400	20.5



statement that "the copper and zinc content seem to be more important in securing high strengths than the factors noted above" (variations in precious-metal content). This is, of course, an observation and not a criticism.

We must call attention to the fact that oven-cooling (whether a good or a bad practice) was outlined by the Bureau of Standards and not by the American Dental Trade Association, as is stated at the top of page 388.

We do not care to enter a discussion of the virtues of the two methods of heat treating discussed, except to point out that oven-cooling does demand a more nearly foolproof alloy and that the values reported above for the superior commercial dental alloys are for oven-cooled specimens. Undoubtedly, for the alloys which the authors are considering, conclusion 5, "the superiority of the fixed temperature aging treatment is demonstrated," is correct. But for dental alloys subjected to various heat treatments such as soldering, vulcanization operations, slow cooling in large masses of insulating investments and in contact with molten cast alloys, the more severe and less critical 30-min. oven-cooling heat treatment is desirable. As is pointed out above, no difficulty is encountered in securing alloys to withstand this treatment, and furthermore, when so treated they are superior to any alloy mentioned in this paper.

Fig. 33 may be misinterpreted, because some may decide that by substituting 25 per cent (atomic) Pd for 25 per cent (atomic) Au it will be possible to reduce the cost more than 40 per cent. A further explanation is desirable, giving cost of metals used, and actual savings if this figure is to remain in the paper.

The paper is an excellent contribution to this field which has been so long neglected. It will undoubtedly assist in the further improvements in the precious-metal alloys used in dental and other arts.

F. E. CARTER, Newark, N. J. (written discussion).—To the best of my belief, this paper covers a range of investigation which has never previously been attempted. In general, it seems that the authors claim to be able to produce alloys of rather simple composition, which will, by proper heat treatment, give all the desired properties—properties which heretofore have been obtained only by very complex compositions. If this is true, it is good news indeed.

It is particularly interesting to study the differences in action of additions of platinum and palladium to the gold alloys; apparently the three main conclusions on this point are: (1) Palladium gives latitude in the aging treatment; (2) palladium gives greater variations in the final strength of the alloys than does platinum; (3) alloys with palladium additions do not show the drop in strength on prolonged heat treatment that is observable where platinum is used.

While it is realized that photographing some of the typical alloys would have meant a great deal of work, the added value of the paper would have been very great. We appreciate the amount of new information in the paper as it is, but hope that at some future time the authors will take a small section of the paper and go into it in detail with photomicrographs, and so forth.

E. M. WISE (written discussion).—The remarks of Messrs. Souder, Paffenbarger and Sweeney seem to have overlooked the fact that the purpose of the second section of the paper was primarily to indicate the important influence of platinum or palladium upon the strength, color and aging characteristics of base alloys of a particular gold content, rather than to develop additional alloys of the rather special high-strength class possessing higher strengths than those now commercially available. As a matter of fact, the application of the alloys of very high strength is restricted to a rather limited field, while a much broader field exists for platinum-metal content alloys of more moderate strength where the addition of platinum or palladium is essential to secure reliable performance and freedom from damage through thermal treatments,

such as those involved in soldering, casting, etc., which would ruin alloys not containing adequate quantities of the platinum group metals.

In an investigation of this nature, it is necessary to select some basis for comparison, and after mature consideration the base alloy containing 50 at. per cent Au, 29 at. per cent Cu, 1 at. per cent Zn, remainder silver, was chosen. The maintenance of the constant total atomic percentage of 50 at. per cent for the gold plus platinum or palladium was considered to be desirable, as this represented the probable lower limit of the domain of alloys useful for dental purposes, and would thus afford a broad basis for supplementary studies at other precious-metal levels which, it is hoped, will be undertaken at some future time.

With a given total atomic percentage of gold plus platinum or palladium and a fixed ratio of platinum metal to gold, variations in the silver to copper ratio will alter the properties, and in particular cases, may well lead to the development of properties in excess of those reported by the authors. This is a broad subject which it is hoped may be studied and reported upon by other investigators.

For the purposes of the present investigation, the silver to copper ratio selected appears to have been quite suitable for alloys possessing a wide range of platinum metal content and to have been quite adequate for indicating the role of the platinum metals in such alloys.

The properties which can be developed in alloys containing both platinum and palladium in conjunction with gold, silver and copper are remarkable and some of the reasons for using such alloys are indicated in the present paper. The excellent results currently obtained with commercial alloys containing both platinum and palladium give some indication of the potentialities of alloys of this latter type.

Our reference to "oven-cool" treatment outlined by the American Dental Trade Association was not intended to imply that this organization originated the treatment. We state only that the method of carrying out the oven-cool treatment was that used by the A. D. T. A. and recorded in reference 38.

The discussers state that alloys which respond satisfactorily to oven-cooling are more nearly foolproof than those that do not. This is undoubtedly the case when the conditions of use approximate those of oven-cooling, but it is the authors' experience that practical treatments often widely depart from the oven-cool cycle; more rapid rates of cooling being common and even slower rates not exceptional. The authors believe that the selection of material for a specific purpose can best be based upon tests which parallel the conditions of use. On the other hand, heat treatments recommended for the purpose of improving physical properties should be those adapted to particular alloys rather than an arbitrary one adapted only to alloys in a limited range of composition.

For specification purposes a treatment which depends upon the characteristics of the furnace used seems to us unlikely to give concordant results in various laboratories and might well be replaced by a constant-temperature aging treatment.

With reference to the savings resulting from the replacement of gold by palladium, the paragraph descriptive of Fig. 33 makes clear that the comparison in costs is based on the relative costs of a structure of constant strength when made from alloys containing various amounts of platinum or palladium. Such a comparison involves the cost per unit weight, the density of the alloy and the strength of the heat-treated alloy, and is based on prevailing prices for the component metals and upon the strengths resulting from aging for 15 min. at the optimum temperatures for the several alloys.

If comparisons are based on the cost per unit volume, without regard to the strength obtained, the cost will decrease continuously as gold is replaced by palladium and will drop to 51 per cent of the cost of the gold-base alloy when all of the gold has been thus

replaced. The metal cost per unit weight also drops continuously as gold is replaced by palladium and drops to 70 per cent of that of the gold-base alloy when all of the gold has been so replaced.

These differences are due to the reduction in density occasioned by the replacement of gold by palladium and are important to the user in view of the fact that the dimensions of structures are determined either by strength or geometric requirements, or sometimes by both factors. As noted in the present paper, the increase in strength occasioned by the introduction of platinum is so great that in structures of constant strength important savings in primary metal cost likewise accrue from its presence.

With regard to comment with respect to conclusion 2, little further can be said, since the limitations of alloys hardened with base metals have been well established and it has become general practice to employ considerable percentages of the platinum group metals where reliability and anything more than very moderate strengths are desired.

An examination of the data in the paper and a consideration of the data in Table I suggests that the addition of platinum metals renders possible the production of alloys possessing satisfactory physical properties at higher precious metal levels than is possible when gold is the only noble metal present.

Replying to Dr. Carter, in the present study the alloys chosen were such that the specific effects of the metals, platinum and palladium, could be demonstrated and their general behavior studied. It is evident that an excellent range of properties can be developed by rather simple alloys and for many purposes of dental restoration these are undoubtedly adequate. For special purposes, notably where very high strengths are required, it is apparent that alloys containing both platinum and palladium in conjunction with gold, silver and copper possess further advantages and will develop properties in excess of those of the quaternary alloys discussed here. However, even these alloys need not be unduly complex.

The authors have prepared photomicrographs of all of the alloys after important heat treatments and plan to present these and other data in the near future. This further information will clarify some of the phenomena brought to light in the physical tests herein reported.

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